were carried out on an AMX600 NMR spectrometer (Bruker, Karlsruhe, Germany) equipped a 5 mm triple-resonance probehead with z-gradients. Edman degradation was performed on a Hewlett–Packard 241 protein sequencer equipped with a biphasic column detector (Hewlett–Packard, Waldbronn, Germany). For amino acid analysis with GC-MS (HP 5973/HP 6890, Agilent Technologies, Waldbronn, Germany), the peptides were hydrolyzed under vacuum (6 N HCl containing 5 % phenol, 110 °C, 24 h) and derivatized with methanol/HCl (2 N, 110 °C, 15 min), trifluoroacetic anhydride (110 °C, 10 min), and then BSTFA/HMDS/pyridine (4:1:4, 80 °C, 30 min; BSTFA = N,O-bis(trimethylsilyl) trifluoroacetamide, HMDS = 1,1,1,3,3,3-hexamethyldisilazane), and analyzed by GC-MS on fused silica capillaries (25 m × 0.25 mm) coated with either L-Chirasil-Val or Lipodex E (30 %) in PS255 (film thickness $d_f = 0.13$ µm). For sugar analysis, SP-1294 was subjected to methanolysis (HCl (0.65 N) in methanol/methyl acetate (4:1), 70 °C, 16 h). The trimethylsilyl derivatives were prepared by using BSTFA/pyridine (1:1, 80 °C, 30 min), and analyzed by GC-MS on an HP 1-MS fused silica capillary (30 m × 0.25 mm; $d_f = 0.25$ µm, Agilent Technologies).

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New Phosphorus Ligands for the Rhodium-Catalyzed Isomerization/Hydroformylation of Internal Octenes

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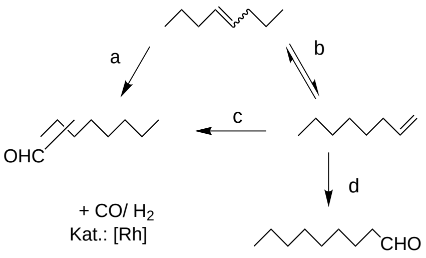
The synthesis of placticizers is closely related to the n-regioselective hydroformylation of olefins. World-wide, propene is an important feed stock in the rhodium-catalyzed synthesis of n-butanal. The use of higher internal olefins, for example di-n-butene from fraction II of the refining process, offers a very interesting and financially attractive alternative that is also used industrially. In these processes the use of unmodified cobalt catalysts and cobalt–phosphane complexes is dominant. At 80–350 bar and 160–190 °C regioselectivities of around 50 % with regard to the desired terminal hydroformylation product are achieved, this can be increased to over 80 % by modifying the catalyst with a suitable phosphine ligand.[1]

The development of a catalyst that delivers high activities and selectivities under mild conditions is not only of industrial importance, Scheme 1 illuminates the scientific problems with the example of 4-octene as a substrate. The catalyst and the reaction conditions must be coordinated so that a dynamic kinetic control of the reaction, based on isomerization to the thermodynamically less stable terminal olefin (step b) occurs and that this olefin rapidly undergoes the final n-regioselective hydroformylation step (d). The formation of the isomeric aldehydes (a, c) is thus suppressed.



Scheme 1. Isomerization and hydroformylation of (Z)/(E)-4-octene.

Recently van Leeuwen et al. reported that with xantphos-type diphosphines rhodium catalysts gave n-nonanal in 86 % regioselectivity from (E)-4-octene.[2] The low isomerization activity of the catalyst however, resulted in turnover frequen-

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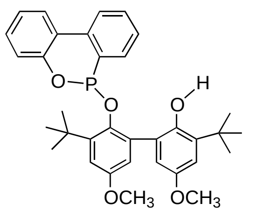

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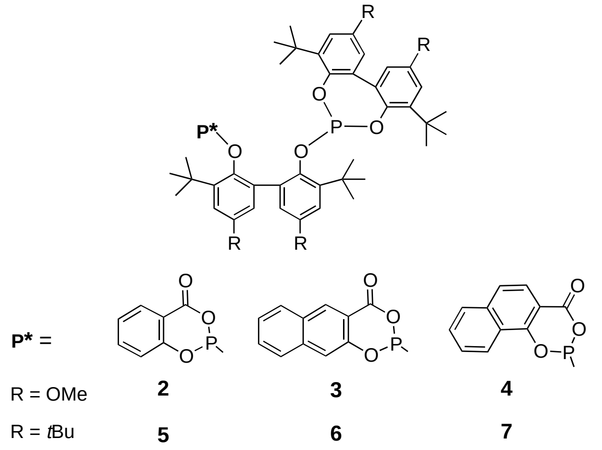
cies of only 15 h^{-1} (112 h^{-1} for 2-octene) and thus no effective control of the reaction. The phosphonite system (Rh/**1**) that we reported recently is less selective than van Leeuwens catalyst, however, under comparatively mild conditions (20 bar/140 °C) it can compete with the unmodified cobalt catalyst in terms of selectivity and activity.[3]

New developments in the rhodium-catalyzed oxo reaction (hydroformylation) of long-chain internal olefins have to show a clear improvement in the *n*-selectivity and a catalytic activity of practical use. Herein we report results that emphasize the astounding potential that π-acid bidentate ligands of unsymmetrical structure have in the hydroformylation of isomers of *n*-octenes.

The ligands **2**–**7** were synthesized. Their most important structural feature, apart from the 2,2′-dioxydiphenyl fragment, known from the work of the firm UCC, is an *O*-acylphosphite moiety. These types of 3-aryloxy-1,3,2-dioxaphosphine-4-ones are readily prepared from the reaction of the corresponding 2-hydroxyaryl carboxylic acid with PCl_3 and subsequent treatment with phenols.[4, 5]



Preliminary attempts to employ the new hybrid ligands in the hydroformylation of 1-octene at 100 °C and 50 bar and with a Rh:P ratio of 1:10 (40 ppm Rh) gave *n*-selectivities with **2** and **3** of 87.4 and 79.0 %, respectively, with an aldehyde yield of around 80 % and complete isomerization of the remaining olefins. Impressively this desired isomerization activity can be used at higher temperatures for the hydroformylation of internal olefins. Table 1 summarizes the results and enables a comparison with **1**. A substrate mixture containing up to 94 % internal olefins was used. The reactions were carried out at 130 °C and under a constant pressure of synthesis gas of 20 bar.

Most noteworthy are the selectivities near an *n*/*iso* ratio of two and the accompanying high catalytic activities. Thus at rhodium concentrations of 1 mmolL^{-1} near to quantitative conversion occurs and at the same time there is very little hydrogenation activity towards the aldehyde. Significant substrate hydrogenation cannot be proven because the amount of octane found in the reaction solution corresponds to that present in the starting mixture. The maximum selectivity, 69 % *n*-nonanal, is obtained with ligand **4**. Comparison of the results clearly shows the influence of the substituents at the periphery of the ligand; *tert*-butyl groups in the 5,5′ position counteract the increasing selectivity with increasing steric bulk caused by the 3-aryloxy-1,3,2-dioxaphosphine-4-one unit.

Table 1. Hydroformylation[a] of isomers of *n*-octene[b] with the bidentate ligands **2**–**7** and the phosphonite **1**.[c]

Ligand	Yield [%][d]	*n*-Nonanal [%][e]	ROH [%][f]	TOF [h^{-1}][g]
2	94	63.9	0.2	> 4600[h]
3	95	64.2	0.2	4310
4	96	69.0	0.3	4448
5	95	67.3	0.1	3119
6	93	67.9	0.1	3324
7	95	68.5	0.2	3336
2[i]	83	64.1	0.2	4751
1[i]	52	47.8	1.4	1320

[a] Experiments were performed in a 200 mL autoclave with $c(n\text{-octene})_0 = 1.68$ M at 130 °C, 3 h in toluene under a constant pressure of 20 bar CO/H_2 (1/1) with [Rh(acac)(cod)] as the catalyst precursor (acac = acetylacetonate, cod = cycloocta-1,5-diene). $c(\text{Rh}) = 1.07$ mM, Rh:P:*n*-octene = 1:10:1570. [b] 3.3 % 1-octene, 48.4 % (*Z*)/(*E*)-2-octene; 29.2 % (*Z*)/(*E*)-3-octene, 16.4 % (*Z*)/(*E*)-4-octene, 2.1 % octene structural isomers, 0.6 % octane. [c] See ref. [3]. [d] Total aldehyde determined by gas chromatography using toluene as the internal standard. [e] Proportion of total aldehyde. [f] Total alcohol, with respect to olefin added. [g] Turnover frequency in (mol aldehyde) (mol catalyst)$^{-1}$ h^{-1} at 20 % conversion, calculation based on the gas consumption; this was determined with a gas-flow meter from Fa. Bronkhorst, Holland, (Hitec gas-flow meter). [h] Measurement limit of the gas-flow meter. [i] $c(\text{Rh}) = 0.107$ mM, $t = 6$ h, $T = 130$ °C (**2**) and 140 °C (**1**).

The results presented here impressively demonstrate, for the first time, the possibility of mainly *n*-selective isomerization/hydroformylation of long-chain internal octenes through rhodium compounds, accompanied by catalytic activities that can be used in practice. This can be achieved through the presence of modifying bidentate ligands and under milder conditions than those of the cobalt catalysis.[6]

Looking back on the results obtained with the catalyst system Rh/**1** this clearly shows that the demand for a simultaneous increase in *n*-selectivity and activity can be satisfied. We imagine that the title reaction here will become a recognized synthetic method in the near future. Also with the 3-aryloxy-1,3,2-dioxaphosphine-4-ones presented here we have introduced a new class of ligands that, to the best of our knowledge, has not yet found use in homogeneous catalysis and has potential for use in other metal catalyzed reactions including stereoselective processes.

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[5] The new compounds were obtained as a mixture of diastereomers and were fully characterized. The experimental details are given in the Supporting Information.

[6] Industrial di-*n*-butene was also used consisting of a mixture of internal and structural isomers of octene. For the individual ligands the selectivities towards conversion into terminal aldehydes are comparable to the values given in Table 1.

A Sol–Gel Route to B_4C[**]

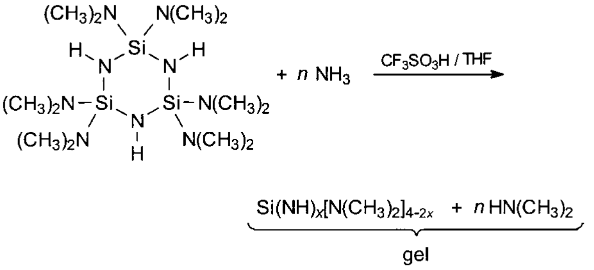
Edwin Kroke,[*] Karl W. Völger,
Alexander Klonczynski, and Ralf Riedel

The classic oxide sol–gel process based on hydrolysis reactions of alkoxides or halides has been examined in detail over several decades.[1] A continuously increasing number of publications indicates that sol–gel processing as a method to produce oxide materials is still gaining importance.[2] In contrast, there have been very few reports on non-oxide sol–gel systems.[3] A sol–gel route to B/(C)/N materials was found in the 1980s by Paine and Narula et al. which is based on "silazanolyses" of *B*-trichloroborazenes with hexa- (HMDS) or heptamethyl disilazane. This sol–gel system was used to prepare B/C/N xerogels, aerogels, and hexagonal boron nitride (h-BN).[4] The crystallization behavior and the oxidation resistance of the products were investigated[5] and molecular model compounds were synthesized and structurally characterized.[6] The results were summarized in a review article and compared with classical routes to boron nitride.[7]

In 1997 it was discovered that chlorosilanes $RSiCl_3$ (with R = H, Cl, alkyl, aryl) form gels in pyridine-catalyzed reactions with bis(trimethylsilyl)carbodiimide.[8] Later, this sol–gel process was extended to dichlorosilanes and functionalized chlorosilanes.[9] Monodisperse spherical particles,[10] Si/C/N coatings and membranes,[11] bulk Si/C/N samples, and pure SiC powder were produced.[12] It is remarkable that this "sol–gel process" is analogous to the oxide system in terms of phenomenological, chemical, physical, and spectroscopic characteristics.[3, 13]

Several attempts to prepare gels from chlorosilanes and HMDS or other silazanes were not successful.[14] Similarly, for carbides or nitrides of elements other than Si, as well as further non-oxide materials such as sulfides, selenides, borides etc., there are very few examples of sol–gel processes known.[3] Most attempts to synthesize non-oxide gels resulted in the formation of solid precipitates.

Recently the first example of a sol–gel process based on ammonolysis has been discovered by Bradley et al., starting from a dialkylamino-substituted cyclic trisilane Si/(C)/N gels were prepared [Eq. (1)].[15]



(1)

B/C/N materials are of interest for several reasons. Novel graphitic ternary phases of these elements may provide materials with properties intermediate between graphite and h-BN.[16] Similarly, sp^3-hybridized B/C/N materials are considered as promising ultra-hard phases combining the properties of diamond and cubic boron nitride (c-BN).[17]

Boron carbide (B_4C) ranks next to diamond in its hardness.[18] It is produced on an industrial scale by classical carbothermal reduction of B_2O_3 in electric arc furnaces. Dense materials are obtained either by pressureless sintering or hot pressing at 2100–2250 °C. B_4C is used for armor plating, blasting nozzles, as mechanical seal faces, and for grinding and cutting tools. The natural presence of the ^{10}B isotope together with chemical inertness and stability under irradiation makes B_4C valuable as a neutron absorber. Because of its ability to generate an electromotive force (EMF) which increases with temperature B_4C has been studied for space power generation and used for high-temperature thermocouples.

In our search for ternary B/C/N phases we examined the reactions of BCl_3 and *B*-trichloroborazene with bis(trimethylsilyl)carbodiimide. It turned out that BCl_3 forms solid, insoluble, and infusible products, which contained either residual chlorine or significant amounts of silicon, depending on the reaction conditions. In contrast, *B*-trichloroborazene ($B_3N_3H_3Cl_3$) reacts with bis(trimethylsilyl)carbodiimide in THF, toluene, or even without any solvent to form non-oxide gels. The xerogels obtained after ageing and drying are practically free of chlorine or oxygen and contain only small amounts of silicon.

The FT-infrared (IR) and Raman spectra clearly indicate the presence of the carbodiimide unit showing the characteristic vibration at 2180 cm^{-1} and 1530 cm^{-1}, respectively.[19] In addition the typical bands for N–H and B–N bonds were observed. Only very weak C–H and Si–CH_3 vibration bands at 2980 cm^{-1} and 1250 cm^{-1} were observed. This corresponds well with the elemental analysis, given in Table 1, that indicate

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