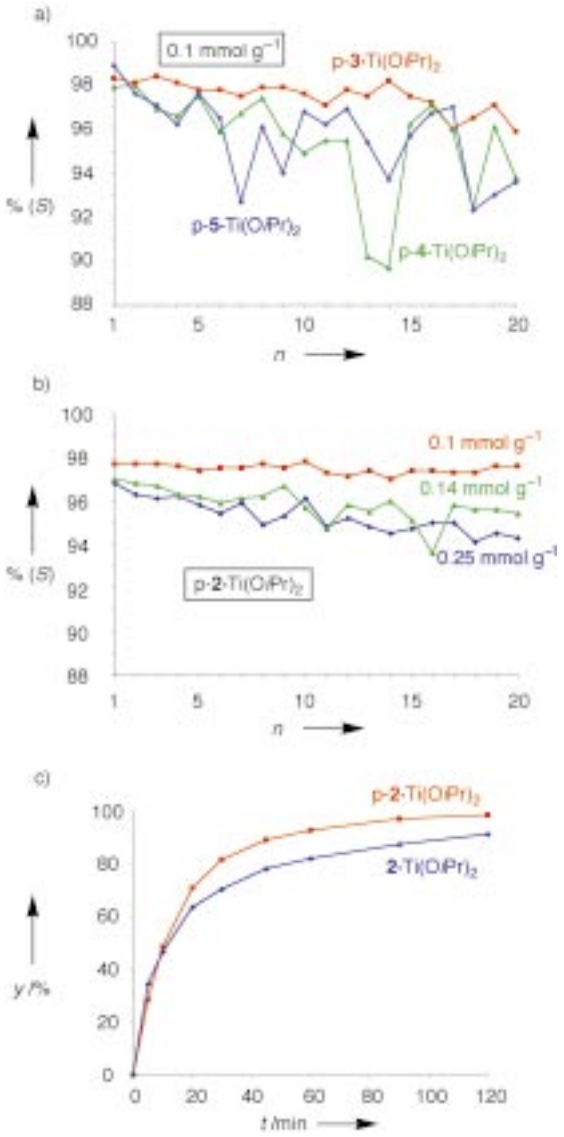

Figure 1. Enantioselectivities in the formation of (*S*)-1-phenylpropanol in *n* catalytic cycles a) with p-**3** · Ti-TADDOLate, p-**4** · Ti-TADDOLate, and p-**5** · Ti-TADDOLate under standard conditions (Scheme 2) and b) with p-**2** · Ti-TADDOLate using loadings of 0.1, 0.14, and 0.25 mmol g^{-1}; c) comparison of reaction kinetics with polymer-bound (red) and with homogeneous (blue) dendritic Ti-TADDOLate (y = conversion).[9]

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Chelated Bisphosphites with a Calix[4]arene Backbone: New Ligands for Rhodium-Catalyzed Low-Pressure Hydroformylation with Controlled Regioselectivity

Rocco Paciello,* Lorenz Siggel, and Michael Röper*

Dedicated to Professor Dr. Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday

The rhodium-catalyzed low-pressure hydroformylation of olefins is, in terms of production volume, one of the most important technical applications of homogeneous catalysis.[1] Rhodium complexes with ligands such as triphenylphosphane lead to aldehydes and especially to their linear isomers in very high yields. Furthermore, they allow the synthesis to be performed under low-pressure conditions, which is advantageous during processing.[2] Industrial laboratories in particular are constantly searching for catalysts with improved properties. At the center of attention are chelating ligands such as bisphosphanes[3] and sterically hindered bisphosphites,[4] which provide active rhodium complexes of a defined structure in a predictable and controlled fashion.

We have been looking for polyols that can be readily prepared and that contain backbones with a defined con-

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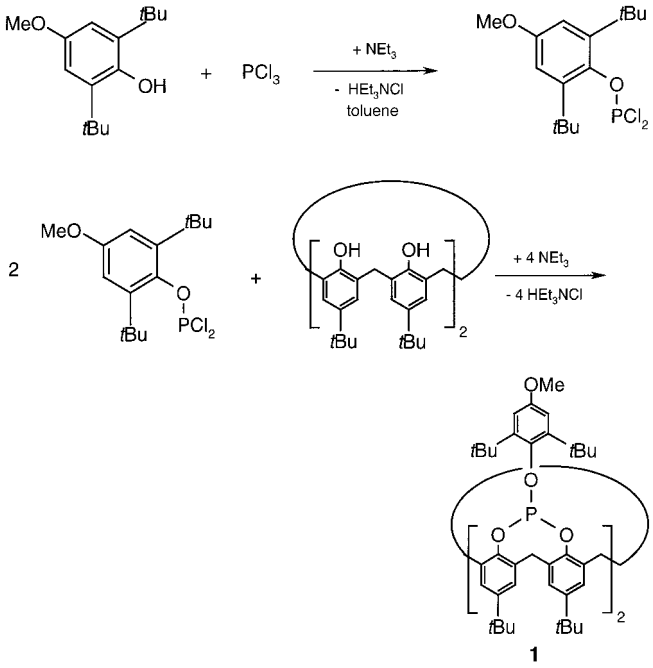
formation for the synthesis of new chelate bisphosphites. During this search we came across calix[4]arenes, which are available in a one-pot reaction in acceptable yields from commercially available precursors such as *p-tert*-butylphenol and formaldehyde.[5] Calix[4]arenes are macrocycles that possess a conical molecular form with four, symmetrically located OH groups at the narrow edge of the cone.[6] Phosphorus-containing ligands based on calix[4]arenes, especially those with phosphane groups, have already been prepared.[7] Recently chelate phosphanes were reported in which the phosphorus atoms are located at the wide edge of the cone. These ligands induce *trans* configurations in square-planar and octahedral complexes of Pd^{2+}, Pt^{2+}, and Ru^{2+}.[8]

We obtained **1** (Scheme 1), the first compound of a new class of chelate phosphites in which two phosphorus atoms each are bonded to two neighboring oxygen atoms of the



Scheme 1. Synthesis of the calixarene bisphosphite **1**.

calix[4]arenes, from the reaction of *p-tert*-butylcalix[4]arene with two equivalents of $P(OAr)Cl_2$ (Ar = 2,6-di-*tert*-butyl-4-methoxyphenyl) in the presence of the base triethylamine.[9] This results in molecular pincers made up of the rigid calix[4]arene backbone and two phosphorus atoms as bonding sites which are further blocked by the sterically demanding aryloxy substituent. The structure of a rhodium complex formed from **1**, as obtained from molecular modeling calculations, is illustrated in Figure 1 (see below).[10]

The hydroformylation of 1-octene with $[Rh(CO)_2(acac)]$/**1** (acac = acetylacetonate) at 20 bar CO/H_2 proceeded relatively slowly (Table 1). A reaction time of eight hours resulted in 63% conversion and an aldehyde selectivity of 61%. The regioselectivity in favor of *n*-nonanal was surprisingly high with 99.5%;[10] GC analysis showed only trace amounts of 2-methyloctanal which could just barely be determined quantitatively. This selectivity corresponds to a ratio of

Table 1. Hydroformylation of 1-octene with Rh/calix[4]arene bisphosphite.[a]

Ligand	Conversion of 1-octene [%]	Selectivity [%]			Nonanal regio-selectivity[10] [%]
		nonanals	*n*-octenes	octane	
1	63 (8 h)	61	12	27	99.5
2	65 (4 h)	75	13	12	96.4
3	53 (4 h)	71	16	13	92.4
4	90 (4 h)	12	82	6	70.0

[a] Conditions: rhodium as $[Rh(CO)_2acac]$, molar ratio olefin:Rh = 4000:1; L:Rh = 5:1; ligand **1**: 20 bar, 100 °C; ligand **2**–**4**: 5 bar, 80 °C.

200:1 between linear and branched aldehydes; to our knowledge, the highest regioselectivities observed to date.

The unusual properties of the catalyst become clear upon analysis of the structure obtained from molecular modeling calculations (see Figure 1).[11] The rhodium atom located at the front side is blocked by the two sterically demanding 2,6-di-*tert*-butylphenoxy substituents in such a manner that even small molecules such as 1-octene are hindered in their attempt to coordinate to the metal center. This results in a relatively low reaction rate. Owing to the steric hindrance, however, the 1-octyl–rhodium intermediate which leads to *n*-nonanal is formed almost exclusively, whereas the sterically more demanding 2-octyl–rhodium intermediate either does not form or does not react to provide 2-methyloctanal.

These results imply that it should be possible to significantly increase the catalytic activity without seriously affecting the regioselectively by decreasing the steric demand in the ligand structure. Replacement of the two *tert*-butyl substituents of the aryloxy group in **1** with isopropyl (ligand **2**), methyl (ligand **3**), and hydrogen (ligand **4**) in molecular modeling calculations resulted in a gradual opening of the structure (Figure 1). A drastic and unexpected structural change occurred upon the transition to **4**: The phenoxy group bends to the side and thus allows an uninhibited approach to the active center.

Based on these results, rhodium complexes with **2** and **3** should be significantly more active than those with the lead structure **1**, while maintaining a very high regioselectivity in

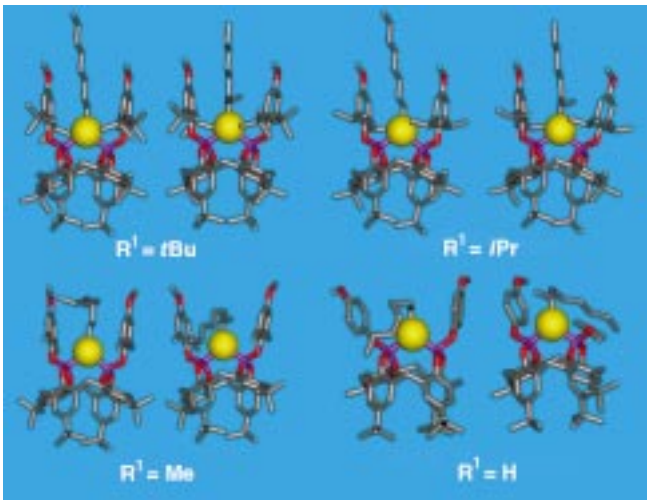


Figure 1. Molecular modeling structures of the rhodium alkyl complexes with **1**–**4**; the structure with the lowest energy is depicted for both the 1-octyl (left) and the 2-octyl adducts (right).

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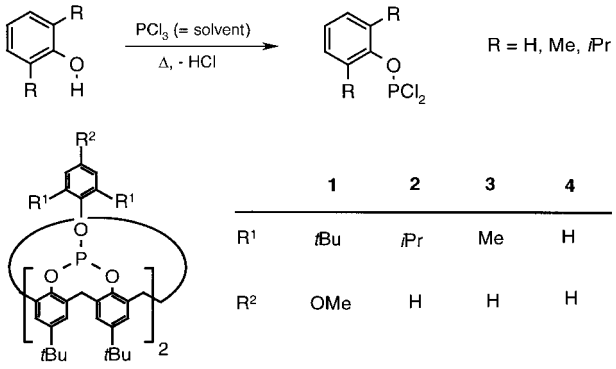
favor of *n*-nonanal. The highest activity is expected for **4**, albeit accompanied by a very low regioselectivity.

During the synthesis of **2**–**4** the preparation of the precursor $P(OAr)Cl_2$ was changed in order to obtain uniform products.[12] Reaction of the phenols in PCl_3 as the solvent, removal of resulting HCl in an argon stream, and removal of excess PCl_3 by distillation resulted in a product (Schema 2) which, without further isolation, could be treated with *p-tert*-butylcalix[4]arene to yield the desired ligands **2**–**4**.



Scheme 2. Synthesis of $P(OAr)Cl_2$ and the calixarene bisphosphites **1**–**4**.

The hydroformylation results with **2**–**4** are summarized in Table 1. Owing to the significantly higher activity, we were able to employ milder conditions than those for the reaction with **1** (5 bar CO/H_2, 80 °C), and also cut the reaction time in half. The ligands **2** and **3** still result in improved aldehyde selectivities, and the regioselectivities of 96.4 % (**2**) and 92.4 % (**3**) are still high.

The calculated structural change upon the transition to ligand **4** manifested itself in catalysis experiments by a high activity for the olefin isomerization, poor aldehyde selectivity, and a very poor regioselectivity of 70 %. Whereas the transition from **1** to **2** and **3** results in only gradual differences, such as a slight decrease in the regioselectivity and a significant improvement in activity, the sterically less demanding ligand **4** leads to a qualitatively different catalyst.

In the rhodium-catalyzed hydroformylation of 1-octene, chelate bisphosphites with a *p-tert*-butylcalix[4]arene backbone lead to *n*-nonanal with surprisingly high regioselectivities.[13] By variation of the structure and use of molecular modeling calculations, it was possible to influence the activity and regioselectivity of the reaction in a controlled fashion. Thus, we have taken a big step towards the idea of rational catalyst design. To be able to treat the electronic properties of ligands in an active complex, and not only the steric factors[14] with molecular modeling calculations as presented herein, we are developing an ab initio process for the catalyst core made up of the rhodium atom and the neighboring atoms in combination with a simultaneous molecular mechanical treatment of the ligand periphery ("embedding" method).

Experimental Section

Syntheses: All reactions were carried out with dry reagents and solvents in flame-dried glassware under an argon atmosphere. Substituted phenols and *p-tert*-butylcalix[4]arene were obtained from Aldrich. They were dried by azeotrope distillation with toluene.

1: First step: 3,5-Di-*tert*-butyl-4-hydroxyanisole (23.6 g, 0.1 mol) was dissolved in toluene (500 mL). The solution was cooled and after addition of triethylamine (68.2 mL, 0.5 mol) transferred into an addition funnel. This solution was added dropwise within 15 min to a solution of toluene (1 L) and PCl_3 (8.8 mL, 0.1 mol) cooled to −40 °C. The mixture was slowly warmed to room temperature, stirred for 1 h at room temperature and then for 10 h at 100 °C. Second step: Powdered *p-tert*-butylcalix[4]arene (32.4 g, 0.05 mol) was added to the solution obtained in the first step, and the mixture was cooled to −40 °C. A solution of triethylamine (136.5 mL, 1 mol) in toluene (500 mL) was added dropwise within 15 min. The solution was slowly warmed to room temperature and stirred for 1 h at room temperature and then for 10 h at 100 °C. The NEt_3HCl precipitate was isolated by filtration through a glass frit and washed with toluene (3 × 250 mL). The filtrate and wash solutions were concentrated at 60 °C and 80 mbar. The light brown, viscous residue was washed with pentane (3 × 100 mL), dried and subsequently extracted with acetonitrile (400 mL) under reflux. After a portion had been dissolved, the remaining powder was filtered, washed with pentane (3 × 200 mL) and dried in vacuo. This procedure afforded 5 g of a white powder (yield 22.5 %). Elemental analysis (%): found: C 75.5, H 8.3, O 10.9, P 5.3; calcd: C 76.2, H 8.9, O 9.9, P 5.1; ^{31}P NMR: $\delta = 121$ (one signal); MS (EI, direct injection): m/z: 1176 [M^+].

2: First step: At room temperature, PCl_3 (21.0 mL, 0.24 mol) was slowly added dropwise to 2,6-diisopropylphenol (7.13 g, 0.04 mol). The solution was subsequently stirred for 5 h under reflux, and excess PCl_3 was removed by distillation. Conversion approx. 94 % (GC). Second step: *p-tert*-Butylcalix[4]arene (13.0 g, 0.02 mol) was dissolved in toluene (1.2 L), triethylamine (55 mL, 0.4 mol) was added and the resulting solution cooled to −20 °C, after which the solution from the first step was added dropwise. The mixture was slowly warmed to room temperature and stirred for 1 h at room temperature and then for 10 h at 100 °C. The NEt_3HCl precipitate was isolated by filtration through a glass frit and washed with toluene (3 × 250 mL). The filtrate and wash solutions were worked up as for **1**. Yield: 11.3 g of a white powder (56 %). Elemental analysis (%): found: C 77.3, H 8.5, O 9.2, P 5.6; calcd: C 77.0, H 8.1, O 9.1, P 5.9; ^{31}P NMR: $\delta = 120$ (one signal).

3: Synthesis as described for **2**, yield 12.4 g of a white powder (65 %). Elemental analysis (%): found: C 76.4, H 7.3, O 10.2, P 6.3; calcd: C 76.0, H 7.4, O 10.1, P 6.5; ^{31}P NMR: $\delta = 119$ (one signal).

4: Synthesis as described for **2**, yield 4.5 g of a white powder (23 %). Elemental analysis (%): found: C 75.2, H 7.1, O 10.9, P 7.2; calcd: C 75.3, H 7.0, O 10.8, P 7.0; ^{31}P NMR: $\delta = 115$ (one signal).

Hydroformylation experiments: A 350-mL autoclave equipped with a gas dispersion turbine was charged with 1-octene (56.9 g, 508 mmol), texanol (70 mL, 2,2,4-trimethyl-1,3-pentanediol isobutyrate), rhodium in the form of $[Rh(CO)_2(acac)]$ (0.032 g, 0.124 mmol), and **1** (0.710 g, 0.604 mmol). After purging with a gas mixture of 50 vol. % CO and H_2 each, the reaction mixture was heated to 100 °C and a pressure of 20 bar applied with this gas mixture. During the reaction the pressure in the reactor was maintained at 20 bar with a pressure controller. After a reaction time of 8 h, analysis of the reaction mixture yielded the following composition (mass proportions, GC, with internal standard and correction factors): 1-octene: 16.6 % (0.188 mol), internal *n*-octenes: 3.41 % (0.039 mol), octane: 7.84 % (0.087 mol), 2-propylhexanal: 0.00 % (0.0 mol), 2-ethylheptanal: 0.00 % (0.0 mol), 2-methyloctanal: 0.11 % (0.001 mol), *n*-nonanal: 21.84 % (0.195 mol), texanol: 45.8 %, other: 0.0 %; conversion (based on 1-octene): 63 %; yields: nonanal: 39 %, octane: 17 %; selectivity (based on 1-octene): nonanals: 61 %, octane: 27 %, internal *n*-octenes: 12 %; regioselectivity[10] *n*-nonanal/nonanals: 99.5 %. The approximate conditions applied for the analogous hydroformylations in the presence of **2**–**4** were a temperature of 80 °C and a total pressure of 5 bar.

Molecular modeling calculations: All calculations were performed using a Silicon Graphics Indigo2 Workstation under a CHARMm21 force field as implemented in the program Quanta (Molecular Simulations Inc., 9685 Scranton Road, San Diego, CA 92121, USA). No restrictive assumptions were made for the geometric environment of the rhodium atom. The chelate bisphosphite and the 1-octyl- or the 2-octyl substituent were bonded to the rhodium atom. Vibrational terms for the bonds between the

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metal center and the attached atoms were set based on crystallographic data, the angle and torsional terms were set to zero. Parameters for the nonbonding terms (Lennard-Jones 6–12) were set by Quanta. For further details see reference [11].

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Organic Transformations at a Group 4 Metallocene Framework: Formation of a Rigid ansa-Metallocene by Mannich-type Carbon–Carbon Coupling

Stephanie Knüppel, Gerhard Erker,* and Roland Fröhlich

Group 4 ansa-metallocenes have been prepared in great structural variety owing to their key importance in homogeneous Ziegler catalysis. In the vast majority of the cases reported the specific ansa bridge and the chosen substitution pattern was built up or incorporated into the preformed organic ligand system before final attachment to the electrophilic Group 4 metal center.[1] Examples for selective organic reactions at the Group 4 metallocene framework, especially those involving conventional organic functional group chemistry, are close to nonexistent,[2] probably because of a pronounced incompatibility of the majority of the air- and moisture-sensitive Group 4 metallocene complexes with the typical conditions involved in many classical C–C coupling procedures in organic synthesis.

We and a few others had previously investigated a number of ways for dealing with functional groups at the bent metallocene nucleus.[3] We have now, to our knowledge for the first time, found a simple way to close an ansa bridge at the preformed Group 4 metallocene complex using a variant of the Mannich reaction, a classical synthetic organic method for forming a carbon–carbon bond.

Our simple route starts with rather conventional fulvene chemistry. O-methylated *N*,*N*-dimethylacetamide (**1a**) was treated with sodium cyclopentadienide according to the procedure developed by Hafner et al.[4] to yield 6-(dimethylamino)-6-methylfulvene (**2a**, Scheme 1). Amine exchange by treatment with, for example, the cyclic secondary amines pyrrolidine, piperidine, or morpholine gave the corresponding 6-amino-substituted fulvenes **2b**–**d**. In some cases the direct route employing the acetamides derived from these cyclic amines proved to be advantageous.

Deprotonation of the fulvene **2a** readily takes place upon treatment with methyllithium (1 molar equiv) in diethyl ether to give **3a**, which was isolated (ca. 90% yield) and characterized spectroscopically (^{13}C NMR ([D$_6$]benzene/[D$_8$]THF 8/1): $\delta = 42.2$ (NMe_2), 157.6 and 81.6 ($C{=}CH_2$), 119.1 (*ipso*-C), 104.6 and 103.7 (CH of C_5H_4); ^{1}H NMR: $\delta = 4.33$ and 3.91 ($^2J = 1$ Hz, $=CH_2$)). The enamino-substituted cyclopentadienides **3b**–**d** were obtained accordingly by treatment of **2b**–**d** with methyllithium. The reagents **3a**–**d** were then treated with titanium, zirconium, or hafnium tetrachloride in a 2:1 molar ratio under carefully selected conditions. The reaction

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