

REGIOSELECTIVE HYDROFORMYLATION OF CITRONELLENE USING A NOVEL RHODIUM-CATALYST

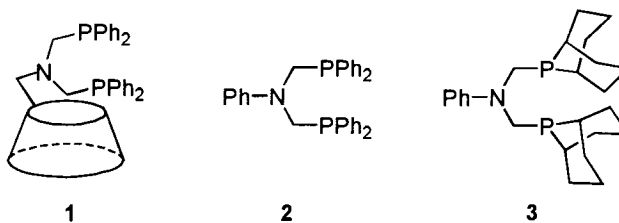
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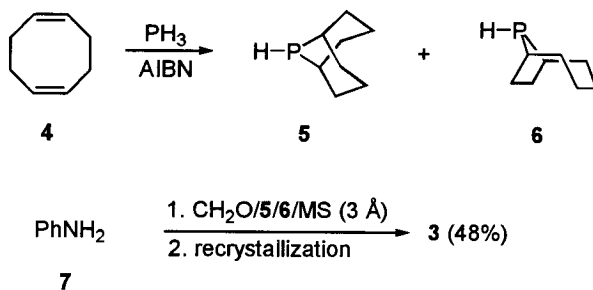
Abstract - The bidentate diphosphine *N,N*-bis-(*P*-(phosphabicyclo[3.3.1]nonan)-methyl)aniline is readily prepared by phosphanomethylation of aniline. It forms a Rh-complex which is a highly regioselective catalyst in the hydroformylation of citronellene.

Recently we described the use of water-soluble β -cyclodextrin-modified diphosphines of the type (1) as ligands in the Rh-catalyzed hydrogenation and hydroformylation of higher olefins in a biphasic system (organic solvent/ H_2O).¹ Due to the supramolecular nature of the Rh-catalyst, an unusually high degree of substrate selectivity was observed. Subsequently the synthesis of the parent compound (2) and the application of the corresponding Rh-complex $2/\text{Rh}(\text{COD})\text{BF}_4$ as a catalyst in the regioselective hydroformylation of simple α -olefins in organic solvents were also reported.²

In the case of dienes in which differences in local steric environment at the two olefinic sites pertain, an additional type of regioselectivity becomes relevant, namely site-selectivity. This problem arises, e.g., in the hydroformylation of certain terpenes.³ In principle, ligand tuning can be used to solve both problems. In this communication we describe the synthesis of the bulky diphosphine (3) and its Rh-complex as well as first applications in regio- and site-selective hydroformylation.



Using a procedure first described by scientists at Shell,⁴ 1,5-cyclooctadiene (4) was reacted with PH_3 in the presence of a radical initiator to form a 2:1 mixture of compounds (5) and (6). Phosphanomethylation, a well-known reaction type,⁵ was then performed using 5/6, aniline (7) and formaldehyde. Under the usual conditions^{2,5} only monophosphanomethylation was observed (^{31}P -NMR: $\delta = -33.2$ ppm). However, upon using molecular sieves (MS) to bind the water (and perhaps to catalyze the reaction) quantitative double phosphanomethylation occurred to form a mixture of bidentate ligands. Recrystallization from toluene provided the desired *N,N*-bis(*P*-(phosphabicyclo[3.3.1]nonane)methyl)aniline (3) in pure form and acceptable yield (48%).⁶



Upon exposing ligand (3) to $\text{Rh}(\text{COD})_2\text{BF}_4$, the desired catalyst $3/\text{Rh}(\text{COD})\text{BF}_4$ was formed and isolated in 85% yield.⁷ The X-Ray structure analysis⁸ reveals a surprising structural element which has not been observed in the literature previously for this type of ligand (Figure 1), namely a boat conformation in which the nitrogen closely approaches the rhodium atom [$\text{N}\cdots\text{Rh}$ 3.28(4) Å], suggestive of a weak $\text{N}\cdots\text{Rh}$ interaction. It should, however, be noted that although the N atom is slightly pyramidal (sum of coordination angles 356°), it lies 0.155(4) Å out of the plane through C1, C2 and C3 *away* from the metal. In contrast, the solid state structure of the analogous Rh-complex of (2) shows a chair conformation lacking any $\text{N}\cdots\text{Rh}$ interaction.²

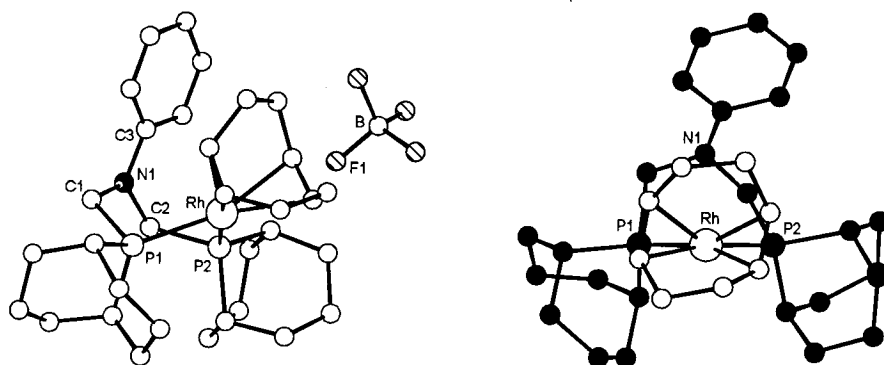
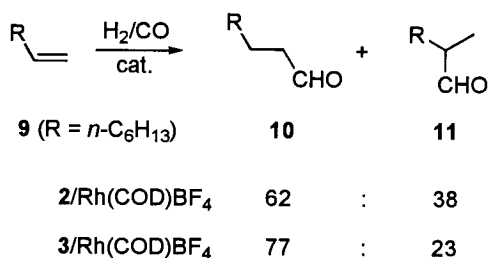


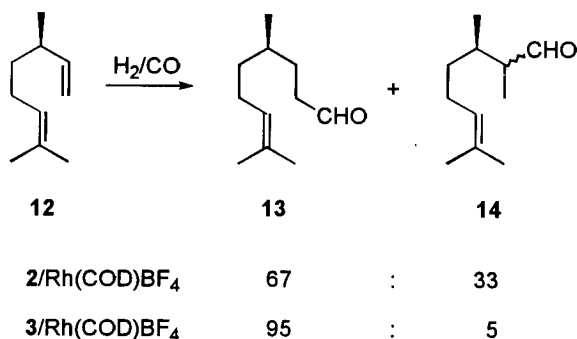
Figure 1

Crystal structure of $3/\text{Rh}(\text{COD})\text{BF}_4$. Left: One of the two almost identical cations in the asymmetric unit and its anion. Selected mean distances (Å) and angles (°): Rh-P1 2.303(11), Rh-P2 2.328(10), $\text{Rh}\cdots\text{N1}$ 3.28(4), P1-C1 1.881(12), P2-C2 1.888(9), N1-C1 1.437(11), N1-C2 1.464(11), N1-C3 1.41(2), P1-Rh-P2 86.3(4), C1-N1-C2 116.3(8), C1-N1-C3 121(2), C2-N1-C3 119(2). Right: View along the axis from the Rh atom to the midpoint of the two P atoms, showing asymmetry of the bidentate diphosphine ligand.

Finally, both $2/\text{Rh}(\text{COD})\text{BF}_4$ and $3/\text{Rh}(\text{COD})\text{BF}_4$ were tested in hydroformylation reactions under the usual conditions² (8 mmol 1-octene, $2.4 \cdot 10^{-5}$ mol ligand, $2 \cdot 10^{-5}$ mol $\text{Rh}(\text{cod})_2\text{BF}_4$, 40 mL toluene, $T = 60^\circ$, $P = 100$ bar ($\text{CO}/\text{H}_2 = 1:1$); conversion > 95%). In the case of 1-octene (9), catalyst $3/\text{Rh}(\text{COD})\text{BF}_4$ showed a somewhat higher degree of regioselectivity in favor of the *n*-aldehyde (10), reflecting increased steric shielding. Indeed, the bicyclic phosphine (5) is believed to be sterically comparable to $\text{HP}(i\text{-Pr})_2$. However, in the case of $3/\text{Rh}(\text{COD})\text{BF}_4$ a small amount of olefin isomerization occurred (10-15%).



In the industrially interesting hydroformylation of citronellene (**12**)^{3,9} an even greater difference between the two catalysts was observed. Whereas **2**/Rh(COD)BF₄ leads to a 2:1 mixture of aldehydes (**13**) and (**14**) after a reaction time of 24 h (after 70 h a complex mixture of isomerized dialdehydes is formed), catalyst **3**/Rh(COD)BF₄ is highly selective. After a reaction time of 70 h under the usual conditions essentially only the desired aldehyde (**13**) is formed selectively. Compounds (**13/14**) are intermediates in the perfume industry.¹⁰



In summary, we have prepared and characterized the novel Rh-catalyst **3**/Rh(COD)BF₄ which shows interesting degrees of regio- and site-selectivity in hydroformylation reactions. The reason for increased selectivity relative to the analog **2**/Rh(COD)BF₄ probably has to do with steric factors.

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6. Procedure for the preparation of **3**: The mixture of paraformaldehyde (1.2 g, 40 mmol), phosphabicyclononanes (2:1 mixture of **5/6** as prepared according to a literature procedure;⁴ 2.64 g, 18.6 mmol), aniline (**7**) (780 μ L, 8.5 mmol) and 6 g of molecular sieves (3 Å) in toluene (50 mL) is stirred at 40 °C for 18 h. A portion of the reaction product crystallizes. After filtration over Celite® and washing 3 times with 30 mL of CH₂Cl₂, the solvent is removed from the combined filtrates. The residue is taken up in hot toluene (20 mL) and placed in a refrigerator. Colorless needles are formed which are collected and dried: 1.65 g of **3** (48%); mp 205 °C (toluene); ³¹P-NMR (CDCl₃): δ = -40.1 ppm; MS(EI): m/z = 401 ([M]⁺, 5%), 260 ([M-C₈H₁₄P]⁺, 30%), 155 ([C₈H₁₆P]⁺, 100%). Anal. Calcd for C₂₄H₃₇NP₂: C 71.79, H 9.28, N 3.48. Found C 71.68, H 9.39, N 3.83.
7. Procedure for the preparation of **3/Rh(COD)BF₄**: The solution of Rh(COD)₂BF₄ (214 mg, 0.53 mmol) in CH₂Cl₂ (10 mL) is treated with ligand (**3**) (212 mg, 0.53 mol) at 0 °C. After 20 min it is attained and the solvent is removed *in vacuo*. The residue is dissolved in CH₂Cl₂ (15 mL) and the mixture is carefully covered with pentane (60 mL). After 4 d the orange/red crystals are collected, washed with pentane and dried *in vacuo* to provide 313 mg (85%) of **3/Rh(COD)BF₄**; mp 180-190 °C (decomp, CH₂Cl₂/pentane); ³¹P-NMR (CDCl₃): δ = 2.04 ppm (d, J_{P-Rh} = 138 Hz). Anal. Calcd for C₃₂H₄₉NBF₄P₂: C 54.95, H 7.06, N 2.00, P 8.55. Found C 54.88, H 6.94, N 1.98, P 8.84.
8. X-Ray analysis of [**3/Rh(COD)**]⁺[BF₄]⁻·[C₃₂H₄₉NP₂Rh]⁺[BF₄]⁻, M_r = 699.38 g mol⁻¹, yellow-orange prism, crystal size 0.14 x 0.21 x 0.54 mm, triclinic, $P\bar{1}$ [No. 2], a = 11.9383(3), b = 16.2172(4), c = 17.6975(4) Å, α = 71.758(1), β = 77.244(1), γ = 75.091(1) °, U = 3107.7(1) Å³, T = 100 K, Z = 4, d_{cal} = 1.50 g cm⁻³, μ = 0.70 mm⁻¹, Siemens SMART CCD diffractometer, λ = 0.71073 Å, ω -scan, 27803 measured reflections, 13874 independent, 10275 with $I > 2\sigma(I)$ (gt.), θ_{max} = 28.0°, no absorption correction, direct methods (SHELX-86, G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.* 1990, **A46**, 467), refinement on F_o^2 (SHELX-93, G. M. Sheldrick, University of Göttingen, 1993), H riding, C atoms isotropic, 419 refined parameters, R_I = 0.097 (gt. data), wR_2 = 0.301 (Chebyshev weights), final shift/error 0.001, residual electron density +2.541 eÅ⁻³ (0.96 Å from Rh). Atomic coordinates and s.u.'s have been deposited at the Cambridge Crystallographic Data Centre, CCDC 118770.
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