REGIOSELECTIVE HYDROFORMYLATION OF CITRONELLENE USING A NOVEL RHODIUM-CATALYST

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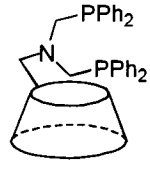
Abstract - The bidentate diphosphine *N,N*-bis-(*P*-(phosphabicyclo[3.3.1]nonan)-methyl)aniline is readily prepared by phosphanomethylation of aniline. It forms a Rh-complex which is a highly regioselective catalyst in the hydroformylation of citronellene.

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**/Rh(COD)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.



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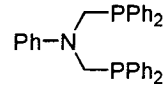

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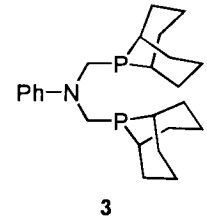

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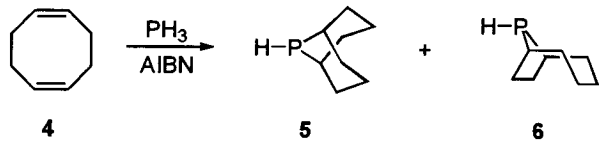
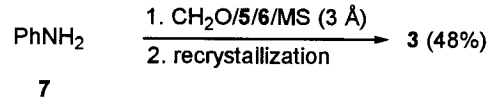
Using a procedure first described by scientists at Shell,[4] 1,5-cyclooctadiene (**4**) was reacted with PH_3 in the presence of a radical initiator to form a 2:1 mixture of compounds (**5**) and (**6**). Phosphanomethylation, a well-known reaction type,[5] was then performed using **5/6**, aniline (**7**) and formaldehyde. Under the usual conditions[2,5] only monophosphanomethylation was observed (^{31}P-NMR: δ = -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]

Dedicated to Professor Teruaki Mukaiyama on the occasion of his 73rd birthday.





Upon exposing ligand (**3**) to $Rh(COD)_2BF_4$, the desired catalyst **3**/$Rh(COD)BF_4$ was formed and isolated in 85% yield.[7] The X-Ray structure analysis[8] 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 [N···Rh 3.28(4) Å], suggestive of a weak N···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 N···Rh interaction.[2]

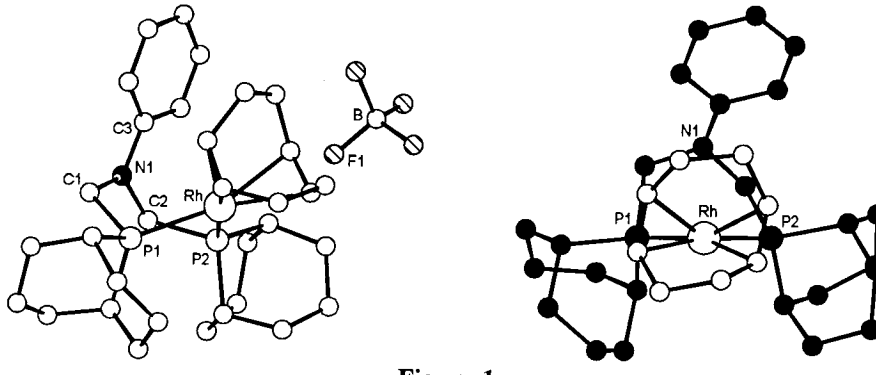
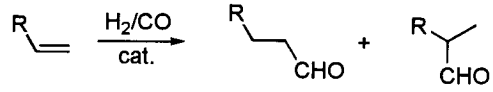


Figure 1

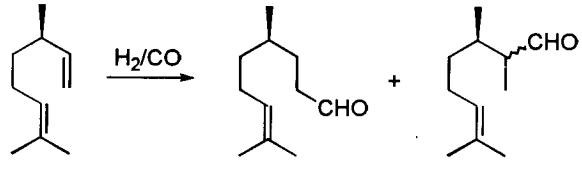
Crystal structure of **3**/$Rh(COD)BF_4$. Left: One of the two almost identical cations in the asymmetric unit and its anion. Selected mean distances (Å) and angles (°): Rh-P1 2.303(11), Rh-P2 2.328(10), Rh···N1 3.28(4), P1-C1 1.881(12), P2-C2 1.888(9), N1-C1 1.437(11), N1-C2 1.464(11), N1-C3 1.41(2), 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**/$Rh(COD)BF_4$ and **3**/$Rh(COD)BF_4$ were tested in hydroformylation reactions under the usual conditions[2] (8 mmol 1-octene, $2.4 \cdot 10^{-5}$ mol ligand, $2 \cdot 10^{-5}$ mol $Rh(cod)_2BF_4$, 40 mL toluene, T = 60°, P = 100 bar (CO/H_2 = 1:1); conversion > 95%). In the case of 1-octene (**9**), catalyst **3**/$Rh(COD)BF_4$ 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 $HP(i\text{-}Pr)_2$. However, in the case of **3**/$Rh(COD)BF_4$ a small amount of olefin isomerization occurred (10-15%).



9 (R = *n*-C_6H_{13})	**10**		**11**
2/Rh(COD)BF_4	62	:	38
3/Rh(COD)BF_4	77	:	23

In the industrially interesting hydroformylation of citronellene (**12**)[3,9] an even greater difference between the two catalysts was observed. Whereas **2**/Rh(COD)BF_4 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)BF_4 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]



12	**13**		**14**
2/Rh(COD)BF_4	67	:	33
3/Rh(COD)BF_4	95	:	5

In summary, we have prepared and characterized the novel Rh-catalyst **3**/Rh(COD)BF_4 which shows interesting degrees of regio- and site-selectivity in hydroformylation reactions. The reason for increased selectivity relative to the analog **2**/Rh(COD)BF_4 probably has to do with steric factors.

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4. Patent DE 1909620 (1969) to Shell (*Chem. Abstr.*, 1970, **72**, 7033); see also J. H. Downing, V. Gel, and P. G. Pringle, *Chem. Commun. (Cambridge)*, 1997, 1527.
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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 µL, 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 CH_2Cl_2, 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); ^{31}P-NMR ($CDCl_3$): δ = -40.1 ppm; MS(EI): *m/z* = 401 ($[M]^+$, 5%), 260 ($[M\text{-}C_8H_{14}P]^+$, 30%), 155 ($[C_8H_{16}P]^+$, 100%). Anal. Calcd for $C_{24}H_{37}NP_2$: 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)BF_4: The solution of $Rh(COD)_2BF_4$ (214 mg, 0.53 mmol) in CH_2Cl_2 (10 mL) is treated with ligand (**3**) (212 mg, 0.53 mol) at 0 °C. After 20 min rt is attained and the solvent is removed *in vacuo*. The residue is dissolved in CH_2Cl_2 (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)BF_4; mp 180-190 °C (decomp, CH_2Cl_2/pentane); ^{31}P-NMR ($CDCl_3$): δ = 2.04 ppm (d, $J_{P\text{-}Rh}$ = 138 Hz). Anal. Calcd for $C_{32}H_{49}NBF_4P_2$: 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)]$^+$[BF_4]$^-$:[$C_{32}H_{49}NP_2Rh$]$^+$[BF_4]$^-$, 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) Å^3, 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_1 = 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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