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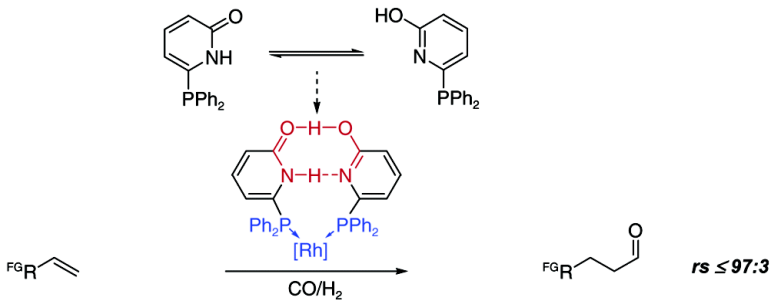


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# Hydrogen Bonding as a Construction Element for Bidentate Donor Ligands in Homogeneous Catalysis: Regioselective Hydroformylation of Terminal Alkenes

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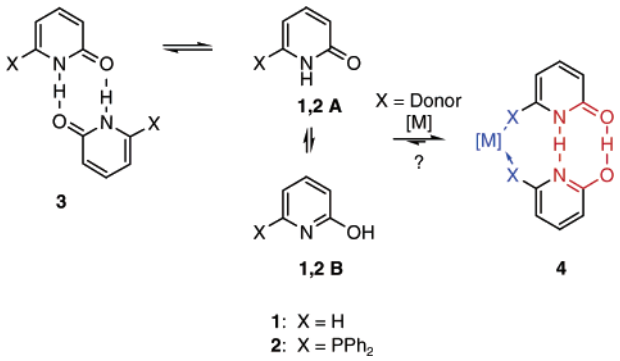
Bidentate donor ligands are essential components of many transition metal catalysts in the homogeneous phase. In contrast to their monodentate counterparts, they often lead to higher levels of regio- and enantioselectivities, which is generally due to the formation of a more rigid microenvironment at the catalytically active metal center and, hence, to a better energetic discrimination of competing reaction pathways.[1] However, in many cases, the covalent connection of the two donor atoms to a suited ligand backbone necessitates a number of synthetic steps which often render the ligand more expensive than the noble metal source.

We herein report on a new concept for the in situ generation of bidentate donor ligands based on the self-assembly of a monodentate ligand in the coordination sphere of a metal center through hydrogen bonding. These new ligands provide highly active and regioselective catalysts for the *n*-selective hydroformylation of terminal alkenes.

The 2-pyridone **1A**/2-hydroxypyridine **1B** tautomer system is known to dimerize in aprotic solvents to form predominantly the symmetrical pyridone dimer **3** through hydrogen bonding (Scheme 1).[2] If X would be a donor atom capable of binding a metal center, a bidentate binding mode would be impossible for dimer **3** for geometric reasons. Alternatively, formation of the mixed dimer between the 2-pyridone and the 2-hydroxypyridine tautomer would generate a ligand architecture suited for a bidentate binding mode **4**. Although this nonsymmetrical dimerization mode is unusual, recent calculations in the gas phase have shown that it is just 4.8 kcal/mol less favorable (X = H) as compared to the commonly observed 2-pyridone dimer.[3] We speculated that if X would be an appropriate donor atom the chelation effect exhibited through coordinative binding to a metal center might overcome this energy penalty to provide the bidentate binding mode **4** as shown in Scheme 1.

***Scheme 1***




For that reason, 6-diphenylphosphanyl-2-pyridone (6-DPPon) **2** was chosen as a first test system. Reaction of 2 equiv of 6-DPPon with [$PtCl_2$(1,5-COD)] gave the *cis*-complex **5**. From the X-ray plot of **5** depicted in Figure 1, it is obvious that the two

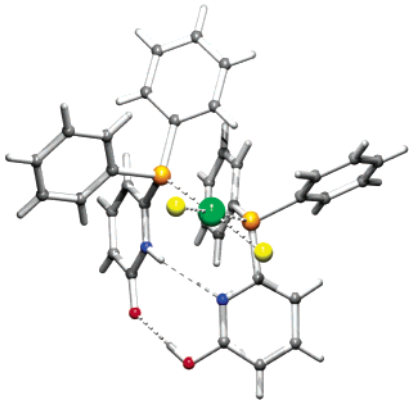


***Figure 1.*** X-ray plot of *cis*-[$PtCl_2$(6-DPPon)$_2$] **5**.

*cis*-coordinated 6-DPPon ligands form the expected hydrogen bonded nonsymmetrical dimer **4** and, hence, act as a chelating ligand for platinum. The significantly different C/N and C/O bond distances within the nitrogen heterocycles confirm that one 6-DPPon ligand exists as the pyridone and the other as the hydroxypyridine tautomer.[4]

To see whether such a chelating binding mode through hydrogen bonding is operative throughout a catalytic reaction, hydroformylation of olefins was chosen as a first test case because a strong chelation effect upon hydroformylation of terminal alkenes is well established.[1a] Thus, only a few tailor-made bidentate ligands such as BISBI,[5] BIPHEPHOS,[6] and XANTPHOS[7] are known to provide good levels of regioselectivity in favor of the linear aldehyde isomer.

As a first test system, hydroformylation of 1-octene was studied. To calibrate the results, the industrially employed rhodium/$PPh_3$ system was selected as the prototype for a monodentate phosphine/rhodium catalyst. As a reference for a bidentate ligand, *t*-Bu-XANTPHOS, one of the best ligands for *n*-selective hydroformylation of terminal alkenes, was chosen.[4,7] As expected, regioselectivity for the rhodium/$PPh_3$ system was rather low (Table 1, entries 1 and 2). A significantly higher regioselectivity is observed for the *t*-Bu-XANTPHOS system. However, catalyst activity is significantly lower (entries 3,4). When employing the 6-DPPon ligand **2**, a catalyst system that performed with both excellent regioselectivity and activity was obtained (entries 5,6). These results indicate that 6-DPPon acts as a chelating ligand. The significantly enhanced activity as compared to that of the *t*-Bu-XANTPHOS system may be due to electronic effects exerted by the electron-withdrawing nature of the pyridone nucleus. Similar activating effects are well documented in hydroformylation.[8]

To study the stability of the intramolecular hydrogen bonding of the rhodium/**2** catalyst, the influence of temperature upon regioselectivity of the hydroformylation of 1-octene was investigated (see Figure 2). Thus, at reaction temperatures between 50 and 110



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***Table 1.*** Hydroformylation of 1-Octene[a]

| entry | ligand | *T* (°C) | conv. (%)[b] | isom. (%)[b] | l:b[b] |
|---|---|---|---|---|---|
| 1 | $PPh_3$ | 65 | 22 | 0.3 | 73:27 |
| 2 | $PPh_3$ | 80 | 98 | 9 | 72:28 |
| 3 | *t*-Bu-XANTPHOS | 65 | 6 | 1 | 98:2 |
| 4 | *t*-Bu-XANTPHOS | 80 | 31 | 2 | 98:2 |
| 5 | **2** | 65 | 56 | 3 | 97:3 |
| 6 | **2** | 80 | 96 | 8 | 96:4 |

[a] Reaction parameters: Rh:L:1-octene (1:20:7000), *c* (1-octene) = 1.4 M, 4 h, toluene, 10 bar $CO/H_2$ (1:1). [b] Determined by GC analysis.

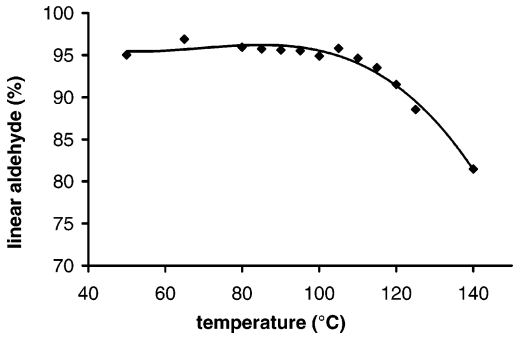
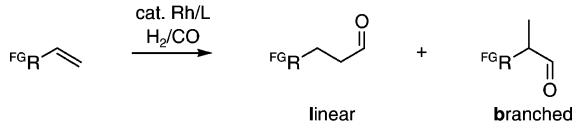



***Figure 2.*** Temperature dependence of *n*-selectivity upon hydroformylation of 1-octene with the 6-DPPon (**2**)/rhodium catalyst.

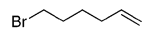
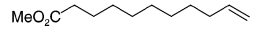
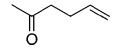
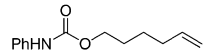
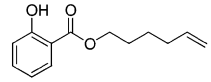
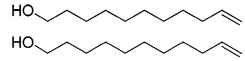
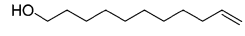
°C, linearity stays high in the range of 95−97%. Above 110 °C, this regioselectivtiy breaks down to values as low as 80%, which is close to the regioselectivity range observed for the monodentate $PPh_3$/rhodium catalyst. These results indicate a continuous erosion of the pyridone hydrogen bonding at temperatures above 110 °C.

The 6-DPPon/rhodium catalyst is operative as a chelation system in the presence of functional groups such as bromides, acetates, esters, and ketones (Table 2, entries 1−4) to give the linear aldehydes in excellent yield (quantitative) and regioselectivity. We next looked at functional groups possessing significant hydrogen bonding capability to learn whether the ligand's hydrogen bonding system may be disrupted. Interestingly, neither a carbamate, a salicylate, nor a free hydroxyl function was able to diminish the high regioselectivity of the rhodium/6-DPPon catalyst (entries 5−8). However, use of an alcoholic solvent or addition of acetic acid resulted in low regioselectivity, which indicated a cleavage of the intramolecular hydrogen bond of the rhodium/6-DPPon catalyst under these conditions (entries 9,10).




In summary, we herein realized a new concept for the construction of bidentate ligands employing self-assembly through hydrogen bonding. Thus, the 6-diphenylphosphino-2-pyridone system **2** forms a chelate in the coordination sphere of a transition metal center through unusual nonsymmetrical pyridone/hydroxypyridine hydrogen bonding. This hydrogen bonding stays intact in a catalytic reaction as proven upon highly regioselective hydroformylation of terminal alkenes. Regioselectivities and reactivities observed

***Table 2.*** Regioselective Hydroformylation of Functionalized Terminal Alkenes with the Rhodium/6-DPPon (**2**) Catalyst in Comparison to the Standard Industrial Rhodium/$PPh_3$ Catalyst

| Entry[a] | substrate | l : b [b] (L = **2**) | l : b [b] (L = $PPh_3$) |
|---|---|---|---|
| 1 |  | 97:3 | 72:28 |
| 2 |  | 96:4 | 71:29 |
| 3 |  | 97:3 | 74:26 |
| 4 |  | 94:6 | 71:29 |
| 5 |  | 96:4 | 69:31 |
| 6 |  | 95:5 | 70:30 |
| 7[c] |  | 95:5 | 89:11 |
| 8 |  | 96:4 | 77:23 |
| 9 |  MeOH as solvent | 83:17 | 77:23 |
| 10 |  + 0.5 equiv. AcOH | 81:19 | - |

[a] Reaction parameters: Rh:L:alkenic substrate (1:20:1000), *c* (alkene) = 0.698 M, toluene, 10 bar $CO/H_2$ (1:1), 70 °C. Full conversion was reached in every case after 20 h. [b] Determined by GC and NMR analysis of crude reaction mixture after 20 h. [c] Isolated as the corresponding $\gamma$-lactol.

rank the 6-DPPon/rhodium system among the most active and regioselective catalysts for the *n*-selective hydroformylation of terminal alkenes.

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**Supporting Information Available:** Experimental details (PDF); crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(1) For selected examples, see: (a) Regioselectivity: van Leeuwen, P. W. N. M.; Casey, C. P.; Whiteker. In *Rhodium Catalyzed Hydroformylation*; van Leeuwen, P. W. N., Claver, C., Eds.; Kluwer Academic Publishers: Dordrecht, 2000; Chapter 4, pp 76−105. (b) Enantioselectivity: Ohkuma, T.; Kitamura, M.; Noyori, R. Asymmetric Hydrogenation. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 2000; Chapter 1, pp 1−110.
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