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Substituent Effects in the Rhodium-catalyzed Hydroformylation of Olefins Using Bis(diarylphosphino)methylamino Ligands

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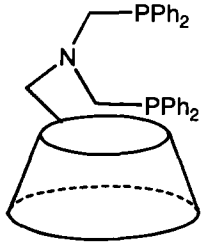
Abstract: Rhodium-complexes of bis(diarylphosphino)methylamino ligands $RN(CH_2PPh_2)_2$ are active catalysts in the hydroformylation of 1-octene and 2-vinylnaphthalene, regioselectivity (n/iso-ratio) and catalyst activity (TOF) depending upon the nature of the para-substituent in the N-aryl moiety (R = C_6H_5, p-CF_3-C_6H_4, p-NMe_2-C_6H_4).

Recently we described the use of water-soluble β-cyclodextrin-modified diphosphanes of the type **1** as ligands in the Rh-catalyzed hydroformylation of higher olefins in an aqueous two-phase system.[1] Since nothing was known concerning Rh-catalyzed hydroformylation based on the parent compounds **2**,[2] we decided to explore this type of ligand in a normal one-phase system[3] and to compare the results with those of the known propano-bridged ligand **3**.[4]



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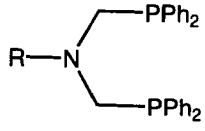
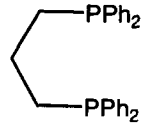


2 a) R = C_6H_5
b) R = p-CF_3-C_4H_4
c) R = p-NMe_2-C_4H_4



3

Compounds **2a-c** were prepared by phosphinomethylation[5] of aniline, p-CF_3-aniline and p-NMe_2-aniline using $PPh_2(CH_2OH)_2Cl$, which resulted in yields of 97 %, 71 % and 93 %, respectively.[3] The corresponding cationic Rh complexes $RN(CH_2PPh_2)_2Rh(cod)BF_4$, prepared by standard reactions involving Rh-bis(cycloocta-1,5-diene)BF_4, were used *in situ* as hydroformylation catalysts.[6] In the case of **2a**, the Rh complex **2a**·Rh(cod)BF_4 was isolated in crystalline form (96 %) and analyzed by X-ray crystallography

(Fig. 1).[7] The metallacycle adopts an approximate chair conformation with a Rh···N distance of 3.797(5) Å, which is too long for a direct interaction (complexation). The P-Rh-P bite angle is 91.8(1)°.

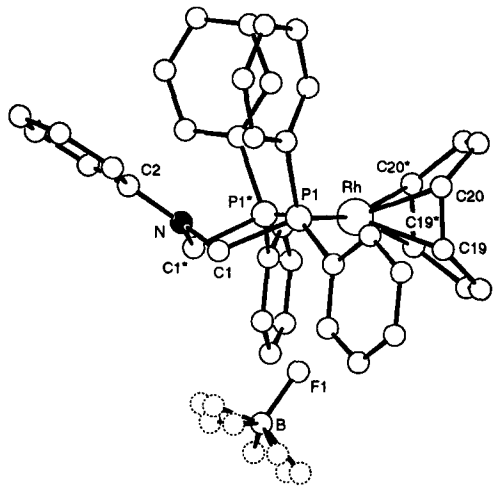
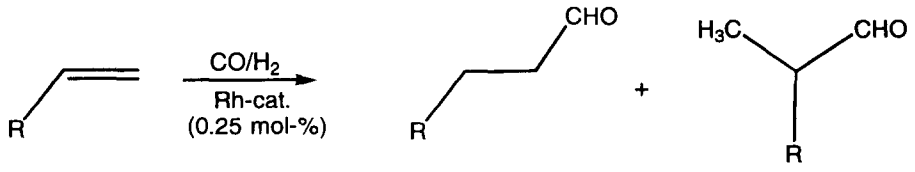


Fig. 1. Crystal structure of **2a**·Rh(cod)BF_4

Hydroformylations[6] of 1-octene (**4a**) and 2-vinylnaphthalene (**4b**) were performed in toluene (60 °C / 100 bar / CO : H_2 = 1 : 1 / 18 h). The alkenes were converted exclusively to the products **5/6**. The results (Table 1) reveal some remarkable trends. In all cases compounds **2a-c** having a nitrogen in the ligand backbone lead to considerably higher catalytic activities than ligand **3** with the all-carbon (propano) bridge, as shown by the TOF numbers. In the hydroformylation of **4a**, the electron withdrawing CF_3 substituent increases the activity, but decreases regioselectivity, whereas the presence of the electron-donating Me_2N substituent results in the opposite effect. In the case of **4b**, which is expected to favor the branched aldehyde **6b**, the CF_3 groups cause a decrease in the TOF number, whereas the Me_2N substituent increases catalyst activity. In the latter case the electron-donating effect of the Me_2N group results in the highest degree of regioselectivity in favor of the branched aldehyde **6b** (Table 1).



4 a) R = n-C_6H_{13} **5** **6**

b) R = 2-naphthyl

Table 1. Hydroformylation[6] of Olefins **4a-b**

Olefin	Catalyst	n/iso[a)] **5 : 6**	TOF (h^{-1})
4a	**2a**·Rh(cod)BF_4	62 : 38	240
4a	**2b**·Rh(cod)BF_4	60 : 40	263
4a	**2c**·Rh(cod)BF_4	65 : 35	185
4a	**3**·Rh(cod)BF_4	63 : 37	57
4b	**2a**·Rh(cod)BF_4	9 : 91	248
4b	**2b**·Rh(cod)BF_4	7 : 93	191
4b	**2c**·Rh(cod)BF_4	5 : 95	436
4b	**3**·Rh(cod)BF_4	7 : 93	161

[a)] Determined by gas chromatography (average of 3 runs; ±1 %).

The above results are not easily explained, especially in view of the fact that detailed kinetic experiments remain to be performed. Indeed, the mechanism of hydroformylation in other systems has been shown to involve a complex series of steps in the catalytic cycle[8], an area of research which has not come to an end. In view of these results the only certain conclusion that we currently draw concerns electronic versus steric effects. Since the para-substituents in ligand **2** are spatially far removed from the catalytic center, steric factors can be safely excluded. Thus, the observed influences on activity and regioselectivity have their origin in electronic effects. Other examples of purely electronic effects of substituents on the outcome of transition metal catalyzed reactions have emerged recently.[9,10] In those cases in which substituted aryl groups are bonded directly to the phosphorus center, the effects can be traced to the different degrees of electron density at the donor position of the ligand.[9] In our system the interpretation is less straightforward because the substituted aryl groups are separated from the phosphorus center by the N-CH_2 unit.

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6. Typical procedure for hydroformylation: In a 50 ml Schlenk tube the mixture of $Rh(cod)_2BF_4$ (1 ml of a 0.02 M CH_2Cl_2-solution corresponding to $2\cdot10^{-2}$ mmol) and a ligand **2** (1 ml of a 0.024 M toluene solution corresponding to $2.4\cdot10^{-2}$ mmol) is stirred under argon at room temperature for 10 min. After addition of an olefin **4** (8 ml of a 1 M toluene-solution corresponding to 8 mmol) the mixture is diluted with toluene to a total volume of 40 ml and forced into a dry autoclave under argon, which is then subjected to 100 bar of CO/H_2 (1 : 1). Stirring is maintained at 60 °C. The kinetics are studied by taking frequent samples via HPLC valve and the contents examined by gas chromatography. The TOF values are determined by graphical means.
7. X-ray analysis of **2a**·Rh(cod)BF_4: $C_{40}H_{41}BF_4NP_2Rh$, M_r = 787.4 g mol^{-1}, orange crystals, crystal size $0.12 \times 0.42 \times 0.21$ mm, orthorhombic, $Cmc2_1$ [No. 36], a = 14.908(1), b = 12.862(1), c = 18.817(1) Å, V = 3608.1(4) $Å^3$, T = 293 K, Z = 4, d_{cal} = 1.45 g cm^{-3}, μ = 0.61 mm^{-1}, Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, ω-2θ-scan, 1967 independent reflections, 1651 observed [$I > 2\sigma(I)$], $[(\sin\theta)/\lambda]_{max}$ = 0.62 $Å^{-1}$, no absorption correction, direct methods (SHELXS-86, Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467), least-squares refinement (on F_o^2, SHELXL-93, Sheldrick, G. M., University of Göttingen, 1993), H riding, F atoms isotropic and disordered (except F1), 233 refined parameters {$\omega = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.7786P]$, where $P = (F_o^2+2F_c^2)/3$}, R_1 = 0.034 (obs. data), wR_2 = 0.084, final shift/error 0.001, residual electron density +0.837/-0.290 $eÅ^{-3}$. Atomic coordinates and e.s.d.'s have been deposited at the Cambridge Crystallographic Data Centre.
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