

Tetrahedron Letters 42 (2001) 643-645

TETRAHEDRON LETTERS

Rhodium-catalyzed hydroformylation of styrene at low temperature using potentially hemilabile phosphite-phosphonate ligands

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Received 10 October 2000; accepted 10 November 2000

Abstract—The synthesis and the effect of phosphite–phosphonate ligands in rhodium-catalyzed hydroformylation of styrene are described. Activity and selectivity of the catalyst are improved, at low temperature, by increasing bulkiness of both phosphite and phosphonate moieties. © 2001 Elsevier Science Ltd. All rights reserved.

Since the studies on RhH(CO)(PPh₃)₃ and hydroformylation of alkenes by Wilkinson and co-workers thirty years ago,¹⁻⁶ extensive studies have been devoted to the search for more active and selective catalysts by ligand modification. Thus, high selectivities in hydroformylation of alkenes have been reported for bulky diphosphine^{7,8} and diphosphite⁹⁻¹⁴ modified Rh-catalysts. complexes have a great potential in homogeneous catalysis since the chelate structure should readily open to liberate a vacant site on the metal. For instance, rhodium complexes with hemilabile phosphine–phosphonate ligands have been shown to have promising catalytic properties which were ascribed to the easy ring opening of the chelate structure by phosphonate moiety decoordination.^{16–20}

On the other hand, there has been an increasing interest in hemilabile chelating ligands:¹⁵ their transition-metal

To our knowledge, no potential hemilabile ligand bear-



Keywords: hydroformylation; styrene; rhodium; hemilabile ligand; phosphite; phosphonate; catalysis. * Corresponding author. Tel.: +33 298016153; fax: +33 298017001; e-mail: herve.desabbayes@univ-brest.fr

Table 1. Rh-catalyzed hydroformylation of styrene²⁵

| Entry | Ligand | 60°C, 1 h | | 25°C, 18 h | |
|-------|-------------------------|-----------------------------|-------|-----------------------------|-------|
| | | Conversion (%) ^a | Iso/n | Conversion (%) ^a | Iso/n |
| 1 | PPh ₃ | 41 | 85/15 | 1 | _ |
| 2 | $Ph_2PCH_2P(O)(OEt)_2$ | 42 | 84/16 | 15 | 99/1 |
| 3 | $Ph_2PCH_2P(O)(OiPr)_2$ | 50 | 86/14 | 30 | 99/1 |
| 1 | $P(OEt)_3$ | 27 | 85/15 | 0 | _ |
| 5 | $P(OPh)_3$ | 92 | 92/8 | 71 | 93/7 |
| 5 | 3a | 56 | 87/13 | 26 | 93/7 |
| 7 | 3b | 90 | 82/18 | 63 | 95/5 |
| 3 | 3c | 93 | 80/20 | 69 | 97/3 |
|) | 3d | 96 | 73/27 | 91 | 97/3 |

^a Converted styrene as percentage of the initial amount. Percentage of aldehydes relative to the converted styrene is >99.

ing both phosphite and phosphonate groups has been studied in catalysis. We now report the syntheses of such ligands and the results obtained in the hydroformylation of styrene with their rhodium complexes as catalyst precursors.

In order to study the influence of each coordinating group (either phosphite or phosphonate) on the catalytic reaction, the four phosphite–phosphonate ligands **3a–d** were prepared by reaction of chlorophosphites 1^{21} with hydroxymethylphosphonates 2^{22} in the presence of diisopropylethylamine (Eqs. (1) and (2)).^{23†}

The catalytic activities of rhodium complexes of ligands **3a–d** on hydroformylation of styrene were compared to those obtained with hemilabile phosphine–phosphonate ligands $Ph_2PCH_2P(O)(OR)_2$ (R = Et, *i*Pr)²⁰ and with PPh₃, P(OEt)₃ and P(OPh)₃. Standard addition of [Rh(Cl)(cod)]₂ with two parts of bifunctional ligands or four parts of monofunctional ligands was used for the catalytic experiments (Eq. (3)). Results are summarized in Table 1.

the activity of the mixed ligands is clearly superior at 25° C.

For the phosphites bearing ethyl groups (entries 4 and 6), it is noteworthy that the presence of a phosphonate moiety leads to better results either at 60 or 25°C. Comparing the results obtained at 60°C with triphenylphosphite (entry 5) and biphenylphosphites (entries 7–9), introduction of a phosphonate group leads to a loss of selectivity, whereas activity is improved by increasing phosphonate bulkiness. On the contrary, at 25°C, increasing the size of phosphonate moiety leads to better conversions and selectivities and ligand **3d** proves to be excellent.

In conclusion, examination of catalytic activity of mixed phosphite-phosphonate ligands on the hydroformylation of styrene has shown promising results, particularly at low temperature. The increased bulkiness of both phosphite and phosphonate moieties leads to improved catalytic activities and selectivities. Synthe-



Table 1 shows the great superiority of the bulky phosphites (entries 5–9), $P(OPh)_3$ giving better results at 60°C and ligand **3d** (entry 9) leading to better activity and selectivity at 25°C.

Concerning the phosphine ligands (entries 1–3), the weak influence of the phosphonate moiety on the catalytic results at 60°C must be noticed, whereas

ses of chiral bulkier mixed phosphite-phosphonate ligands and screening of their potential in asymmetric catalysis are now under investigation.

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 $^{^{\}dagger}$ To our knowledge, only ligand **3a** was previously synthetized by Ivanov according to another procedure.²⁴

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