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Preliminary Communication

Rhodium catalysed hydroformylation using slim phosphate ligands to improve selectivity

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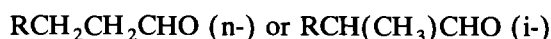
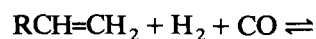
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Abstract

Catalysts based on $[\text{Rh}(\text{R}^1\text{COCHCOR}^1)(\text{CO})_2]$ and a phosphite are active for hydroformylation of hex-1-ene under very mild conditions; very bulky phosphites such as $(2\text{-}^i\text{Bu-4-MeC}_6\text{H}_3\text{O})_3\text{P}$, **3**, give much olefin isomerisation, while the slim caged phosphite ligands, $\text{P}(\text{OCH}_2)_3\text{CR}^2$, show high regioselectivity towards formation of $n\text{-C}_6\text{H}_{13}\text{CHO}$.

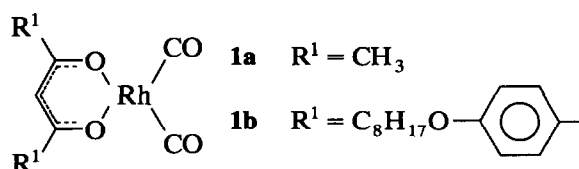
The ordering processes which lead to liquid crystalline character should also be able to direct chemical reactions. The effects of liquid crystalline media on organic reactions have been reviewed by Weiss [1]. Since reactions of metal complexes are often more sensitive to ligand effects, a greater selectivity may be expected in metal-promoted organic reactions as a result of greater ordering of the transition state. There are considerable technical difficulties associated with carrying out reactions and making measurements on them in liquid crystalline media [1], and we have therefore begun to investigate the possibility of controlling metal-catalysed reactions using slim ligands. Slim, rod-like ligands and complexes derived from them often form (calamitic) liquid crystalline materials [2].

Rhodium-catalysed olefin hydroformylation, carried out commercially in the presence of a Rh^1 precursor and a large excess of triphenylphosphine, gives acceptable rates (at *ca.* 100°C and a total CO plus H_2 pressure of 20 atm) and good *n*-/*i*-ratios.

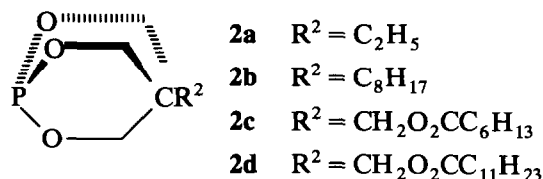


Catalysts based on triaryl phosphites have also been reported [3,4], most recently using very bulky phosphites (with cone angles $\sim 175^\circ$, *e.g.* **3**), by the Union Carbide [5] and Shell groups [6]. These studies indicated that three species were present, $[\text{Rh}(\text{L})_3(\text{CO})\text{H}]$, $[\text{Rh}(\text{L})_2(\text{CO})_2\text{H}]$, and $[\text{Rh}(\text{L})(\text{CO})_3\text{H}]$, the predominant one depending on the nature of the phosphite, L, and the conditions.

We here report a comparative study of catalysts based on $[\text{Rh}(\text{R}^1\text{COCHCOR}^1)(\text{CO})_2]$, **1**, plus ligands (L), including slim phosphites based on the Verkade bicyclic compounds, $\text{P}(\text{OCH}_2)_3\text{CR}^2$, **2** [7,8], as well as the bulky phosphite, **3**, for the hydroformylation of hex-1-ene under very mild standard conditions (50°C; 6 h; 1 atm total pressure, $\text{H}_2:\text{CO}$, 1:2; toluene solution; $[\text{olefin}]/[\text{L}]/[\text{Rh}]$ 250:7:1). The amounts of isomerisation (to internal hexenes), of hydroformylation, and the ratio of heptanal (*n*-) to 2-methylhexanal (*i*-) which they give, are reported in Table 1. No hexane or heptanols were formed under these conditions.



Neither changes in the β -diketonate ligand of the rhodium(I) catalyst precursors, $[\text{Rh}(\text{R}^1\text{COCHCOR}^1)(\text{CO})_2]$ **1a** ($\text{R}^1 = \text{Me}$) and **1b** ($\text{R}^1 = 4\text{-octyloxyphenyl}$), (Table 1; runs 1 and 2, *etc.*), nor the addition of excess $\text{R}^1\text{COCH}_2\text{COR}^1$ ($\text{R}^1 = 4\text{-octyloxyphenyl}$) made significant difference to the hydroformylation reaction. Thus the β -diketone plays little direct role and does not substantially influence the structure of the reaction medium either.



Comparable amounts of aldehydes (runs 1–8 and 10–13; ranging from 17–29%, average 22%) were formed during the 6 h of the measurement from the phosphite cocatalysts **2a–2d**, **3**, and $\text{P}(\text{OPh})_3$. Triphenylphosphine was not a useful ligand for catalysis under the conditions used nor, surprisingly, was tri-

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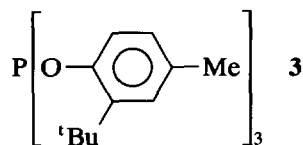
* Dedicated, with best wishes, to Professor Gian Paolo Chiusoli in recognition of his important contributions to organometallic chemistry and its applications to organic synthesis.

TABLE 1. The hydroformylation of hex-1-ene^a

Run	Catalyst	Ligand ^b	Aldehydes (%)	n-/i-	Isomerisation (%)
1	1a	2a	21	6.3	8
2	1b	2a	29	6.7	11
3	1a	2b	26	6.4	16
4	1b	2b	20	8.8	7
5	1a	2c	25	9.8	15
6	1b	2c	21	9.5	13
7	1a	2d	17	8.0	13
8	1b	2d	22	8.2	12
9	1b	P(OEt) ₃	2	5.0	3
10	1a	P(OPh) ₃	17	5.9	25
11	1b	P(OPh) ₃	21	7.3	25
12	1a	3	23	1.2 ^c	75
13	1b	3	21	1.1 ^d	77
14	1b	PPh ₃	5	6.3	4

^a Standard conditions: 50°C; 6 h; 1 atm total pressure (H₂:CO, 1:2); toluene (4 cm³), hex-1-ene (1.2 cm³, 10 mmol); molar ratio [olefin]/[L]/[Rh] 250:7:1. The reactions were analysed and followed by GC (Perkin-Elmer 8700 chromatograph, fid detector, He carrier gas, CPSil 5CB capillary column (50m), n-octane internal standard) and by NMR and IR spectroscopy. Each run was repeated at least twice; mean values are quoted. Yields were reproducible within ±10% of the values given and the reproducibility of the n-/i-ratios was better than ±5% of the values given. ^b Cone angles [9]: 2a–2d 101°, P(OEt)₃ 109°, P(OPh)₃ 128°, PPh₃ 145°, 3 175°. ^c 2-Ethylpentanal (t-) also formed; ratio n-/t- 7.3. ^d 2-Ethylpentanal also formed; ratio n-/t- 4.2.

ethyl phosphite, since its cone angle and electronic character are close to those of 2.



The slim phosphites 2a–2d showed advantages over the others since they gave substantially less isomerisation to internal hexenes (average, 12%; runs 1–8) than either triphenyl phosphite (25%; runs 10, 11) or the bulky phosphite 3 (76%; runs 12, 13). They also showed higher n-/i- aldehyde ratios, in the range 6–10, while catalysts based on the bulky phosphite 3 were rather indiscriminating, and gave n-/i- only slightly larger than 1.0 (and also substantial amounts of the other internal aldehyde, 2-ethylpentanal, t-). Under these (standard) conditions, the best combination involved the ester phosphite 2c, which gave n-/i- close to 10. Most interesting is the observation of some improvement of n-/i- ratio with longer phosphite tail length, maximised at 2c.

GC studies of the change in composition during a reaction showed the following relative turnovers, (i) for hex-1-ene conversion: 43, (2a); 54, (P(OPh)₃); and 103, (3) {mol (mol[Rh])⁻¹ h⁻¹}; (ii) for n-heptanal forma-

tion: 24, (2a); 20, (P(OPh)₃); and 6, (3) {mol (mol[Rh])⁻¹ h⁻¹}; and (iii) for 2-methylhexanal formation: 1.5, (2a); 0.5, (P(OPh)₃); and 8, (3) {mol (mol[Rh])⁻¹ h⁻¹}. Thus while the complexes based on ligand 3 converted hex-1-ene more than twice as fast as those based on 2a, most of the reaction was isomerisation to internal hexenes, and hydroformylation leading to n-heptanal was actually four times as fast with ligand 2a as with 3. Reaction rates with triphenyl phosphite as co-ligand were in between those with 2a and 3.

A similar set of experiments, under the same conditions, with hex-2-ene, showed it to be converted into products six times as fast with the bulky ligand 3 as with 2a. In this case all the aldehydes were formed between 5 and 8 times faster with 3 than with 2a.

The high rates of isomerisation caused by ligand 3 and the relatively high rates of hydroformylation of the internal olefins explain why the n-/i- ratios arising from ligand 3 were so poor, by comparison with those from 2a or triphenyl phosphite.

It seems likely that the most prevalent species for the slim phosphite catalysts are [Rh(L)₃(CO)(H)], which are less potent isomerisation catalysts than the complexes arising from the bulky phosphites (*e.g.*, 3), such as [Rh(L)(CO)₃H] [6].

A high molar ratio [2a]/[Rh] or [P(OPh)₃]/[Rh] led to a high n-/i- aldehyde ratio, and less isomerisation. However, catalysts based on ligand 3 showed scarcely any concentration dependence. This must be due to formation of different complexes at different L/Rh ratios for the first two, while there is only one complex present for 3.

Changes in *p*(H₂):*p*(CO) ratios 1:5 to 1:1 to 5:1 caused only small differences in the percentage of isomerisation of hex-1-ene (from 86% to 74% to 83%) in reactions catalysed by 3; this was accompanied by some change (12% to 25% to 15%) in the aldehyde formation but no change in n-/i- ratio. By contrast, there was a sharp rise in both the amount of olefin isomerisation (50% for 2a, and 63% for triphenyl phosphite, at 5:1 H₂:CO), and in the n-/i- ratios which increased dramatically (4.5 to 5.7 to 34.4 for 2a, and 5.9 to 11.9 to 102.6 for triphenyl phosphite at H₂:CO of 1:5, 1:1, and 5:1 respectively). However, the percentage aldehyde formation was again a maximum at a 1:1 H₂:CO ratio for all three ligands. Increase in total gas pressure (up to 9 atm) increased the total aldehyde formation (accompanied by a slight decrease in n-/i-ratios), but did not increase the amount of isomerisation.

Thus we can conclude that in rhodium-catalysed hydroformylation the slim phosphite ligands 2 repress olefin isomerisation by comparison with the bulky phosphite 3 and with triphenyl phosphite, while the

longer tails of the slim phosphites can also enhance n-/i- aldehyde ratios. This indicates that slim ligands do have promise as co-catalysts. However, the conditions must be very carefully defined; for example, ligand effects can be masked by other factors such as the ratio $p(\text{H}_2):p(\text{CO})$.

Acknowledgements

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- 8 CAUTION: Compounds closely related to the bicyclic phosphites **2** are highly toxic (E. M. Bellet and J. E. Casida, *Science*, **182** (1973) 1135; *Toxicology and Applied Pharmacology*, **47** (1979) 287). Thus we recommend that great care is exercised in handling such materials; contact with the skin should be avoided and they should not be inhaled.
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