Selective Hydroformylation with a Recoverable Dirhodium μ-Thiolato Complex

J. C. Bayón,*[a] J. Real,[a] C. Claver,*[b] A. Polo,[b] and A. Ruiz[b]

[a] *Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain*
[b] *Departament de Química, Facultat de Química de Tarragona, Universitat de Barcelona, Pza. Imperial Tarraco 1, 43005 Tarragona, Spain*

The dimeric precursor complex $\{Rh_2[\mu\text{-}S(CH_2)_3N(Me)_2]_2(cod)_2\}$, (cod = cyclo-octa-1,5-diene), with PPh_3 catalyses the hydroformylation of hex-1-ene, under mild conditions, into heptanals with high yields and selectivities; owing to the presence of the amine group the rhodium catalyst can be quantitatively recovered from the reaction mixture by adding dilute H_2SO_4, and reused without loss of activity.

In recent years Kalck and co-workers have reported the use of dinuclear rhodium thiolates as hydroformylation catalysts.[1]

Our objectives are the recovery of the expensive catalyst and the improvement of the activities and selectivities. The use of a catalyst with strongly co-ordinating μ-thiolato ligands allows chemical modifications as a strategy to achieve these goals. Here we report the synthesis, characterisation, and catalytic results for the new dimeric complex $\{Rh_2[\mu\text{-}S(CH_2)_3N(Me)_2]_2(cod)_2\}$ (**1**), (cod = cyclo-octa-1,5-diene). Chemical and spectroscopic evidence shows that the amino group is not co-ordinated.†

The catalyst precursor (**1**) was used with different molar ratios of phosphorus ligands for the hydroformylation of hex-1-ene as a model substrate, under mild temperature and pressure conditions (80 °C and 5×10^5 Pa). In Table 1 we report conversions and selectivities of linear aldehydes. The best results are obtained with an excess of triphenylphosphine/complex (**1**) in the molar ratio 40/1, where selectivity increases up to 93% in linear aldehyde without a significant decline in activity (87%). As a control experiment the catalytic reaction was carried out with $RhH(CO)(PPh_3)_3$ under the same conditions. A conversion of 66% was achieved with a selectivity of 64% in linear aldehyde. When an excess of PPh_3 was used ($PPh_3/Rh = 20$) the conversion significantly decreased to 43% while the selectivity increased to 80%.

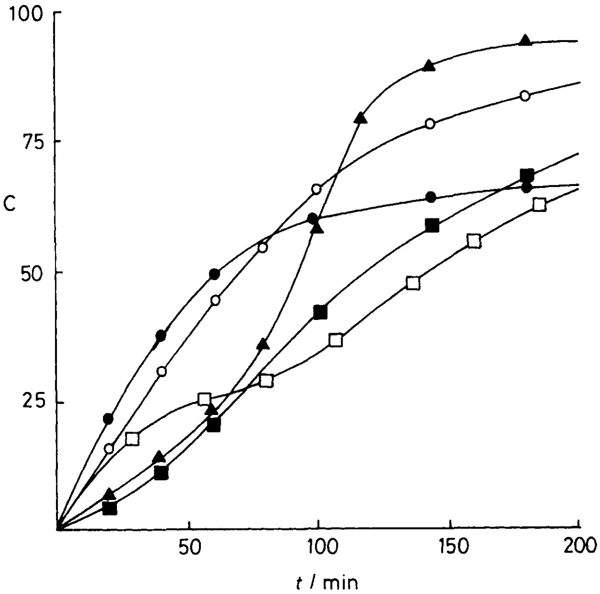
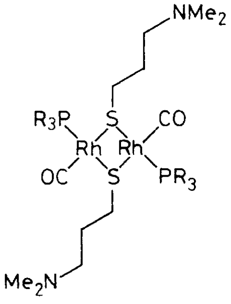


Figure 1. Conversion of hex-1-ene into aldehydes *vs.* time. Reaction conditions are indicated in Table 1 [▲ $PPh_3/(\mathbf{1}) = 4$; ○ $PPh_3/(\mathbf{1}) = 40$; ■ $P(OPh)_3/(\mathbf{1}) = 2$; ● $P(OPh)_3/(\mathbf{1}) = 4$; □ $RhH(CO)(PPh_3)_3$].

---

† A satisfactory elemental analysis was obtained. ^1H n.m.r. 400 MHz ($CDCl_3$): δ 4.15 (br., 8 H, CH, cod); 2.38 (br. m, 8H, CH_2, cod), 1.97 (pseudo d, 8 H, CH_2, cod), 2.13 [s, 12 H, $N(Me)_2$], 2.26 (t, 4H, NCH_2), 2.04 (t, 4H, SCH_2), 1.64 (quint., 4H, $CH_2C\mathit{H}_2CH_2$); $^{13}C\{^1H\}$-gated n.m.r. 100 MHz ($CDCl_3$): δ 79.06 (br. d, $^1J_{CH}$ 161 Hz, CH, cod), 31.47 (t, $^1J_{CH}$ 128 Hz, CH_2, cod), 45.39 [q, $^1J_{CH}$ 133 Hz, $N(Me)_2$], 58.91 (t, $^1J_{CH}$ 132 Hz, NCH_2), 30.48 (t, $^1J_{CH}$ 128 Hz, SCH_2), 22.47 (t, $^1J_{CH}$ 137 Hz, $CH_2CH_2CH_2$).



(A)

Table 1. % of hex-1-ene converted and, in parentheses, amount of heptanal as % of total aldehyde formed.[a]

PR_3/(**1**) molar ratio	R = Ph	R = OPh	R = OMe
2	90 (59)	92 (59)	15 (74)
4	93 (69)	70 (90)	62 (84)
10	93 (84)	26 (84)	20 (83)
20	90 (79)	—	—
40	87 (93)	—	—

[a] *Reaction conditions*: hex-1-ene (40 mmol) and catalyst precursor (0.1 mmol) in 1,2-dichloroethane (15 ml); CO/H_2 = 1, total pressure 5×10^5 Pa at 80 °C.

The catalytic results using (**1**) plus phosphite ligands are significantly different. They exhibit lower performances in terms of activity *vs.* selectivity. Figure 1 shows the evolution of the reaction with time. Maximum conversion is usually achieved in about 3 h. When the reaction is nearly complete the rate decreases owing to the exhaustion of the substrate. The addition of more alkene causes the reaction to restart immediately. G.c. and n.m.r. (^{13}C and ^1H) spectroscopic analysis of the final solutions indicated that aldehydes are the only products formed. No isomerisation or hydrogenation was observed, except when the largest excess of phosphine was used, in which case only traces of alcohol (<0.5%) were detected.

After the catalysis experiments, the final solutions were investigated by Fourier transform i.r. spectroscopy. In all cases a single, strong, CO stretching absorption was observed between 1960 and 2020 cm^{-1}, consistent with a dinuclear μ-dithiolato mixed *trans*-carbonyl phosphine (phosphite) species (A), as previously observed with related systems.[2]

Addition of dilute aqueous sulphuric acid to the reaction mixture causes the immediate and complete precipitation of the catalyst as the yellow ammonium sulphate salt, as compared with an independently prepared sample of $\{Rh_2[\mu\text{-}S(CH_2)_3NH(Me)_2]_2(CO)_2(PPh_3)_2\}SO_4$ [ν_{CO} (KBr) 1974 cm^{-1}]. The solid is insoluble in water and common organic solvents, but the catalyst can be easily and quantitatively regenerated by addition of aqueous base and extraction with an organic solvent. The solution of the catalyst thus obtained can be reused without loss of activity. The isolation of the sulphate salt confirms the presence of the dinuclear complex at the end of the catalytic cycle. This suggests that further modifications of the bridging thiolato ligand can prove useful in the fields of phase transfer, polymer anchoring, and asymmetric hydroformylation.

Attempts to isolate the catalyst as a hydrochloride were unsuccessful owing to the higher solubility of this salt. Also, the presence of halide ions has a deleterious effect on the catalysis; the addition of NBu_4X (X = Cl, Br) to a working system causes immediate quenching. Preliminary i.r. experiments suggest that a five-co-ordinated rhodium species is formed with the halide.[3]

We thank CAICYT (Project PB85-0008-C00) and CIRIT for financial support.

Received, 9th January 1989; Com. 9/00166B

References

1 Ph. Kalck in 'Organometallics in Organic Synthesis,' eds. A. de Meijere and H. tom Dieck, Springer-Verlag, Berlin Heidelberg, 1987, pp. 297—320.

2 Ph. Kalck, J. M. Frances, P. M. Pfister, T. G. Southern, and A. Thorez, *J. Chem. Soc., Chem. Commun.*, 1983, 510; J. C. Bayón, P. Esteban, J. Real, C. Claver, and A. Ruiz, *J. Chem. Soc., Dalton Trans.*, in the press.

3 To be published.