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A NEW STOICHIOMETRIC HYDROFORMYLATION OF OLEFINS MEDIATED BY $HCo_3(CO)_9$

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Summary

3,3-Dimethylbutene is converted into 4,4-dimethylpentanal at −15°C in the presence of $HCo_3(CO)_9$ and $HCo(CO)_4$ under argon. Under the same conditions there is no reaction in the presence of $HCo(CO)_4$ alone. Labeling experiments show that in the formed aldehyde the hydrogen atom of the formyl group has come from the mononuclear complex, and the hydrogen atom of the alkyl moiety from the trinuclear cluster.

Introduction

Cobalt tetracarbonyl hydride (I), dicobalt octacarbonyl (II), and the unsaturated trinuclear hydride $HCo_3(CO)_9$ (III) were shown previously to be related by the equilibrium expressed in eq. 1 [1]:

$$HCo(CO)_4 + Co_2(CO)_8 \rightleftarrows HCo_3(CO)_9 + 3\ CO \qquad (1)$$

More recently the intermediacy of III in the isomerization of olefins induced by mixtures of I and II has been demonstrated [2]. We now report that III, in combination with I, converts olefins stoichiometrically into aldehydes at low temperature. This suggests that III could also play a role as an intermediate in the stoichiometric hydroformylation promoted by I and II.

Experimental

Analytical methods

The organic products were identified by comparison with authentic samples using combined gas chromatography/mass spectrometry. Quantitative determinations were

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by gas chromatography. The overall deuterium incorporation was determined by mass spectral analysis of the aldehyde and more accurately, by comparison of the mass spectrum of the alcohol obtained by reduction with $LiAlH_4$ with that of standard samples of 4,4-dimethylpentanol and 4,4-dimethyl-1-pentanol-1-d_1 (prepared by $LiAlD_4$ reduction of 4,4-dimethylpentanal). The deuterium incorporation in the formyl group was determined by IR analysis, using n-heptanal as an internal standard, from the relative intensities of the 1722 cm^{-1} band of CDO and the 1734 cm^{-1} band of CHO. The deuterium distribution was confirmed by mass spectral analysis of the ester obtained by successive treatments of the reaction mixture with silver oxide and diazomethane.

Stoichiometric hydroformylation of 3,3-dimethylbutene

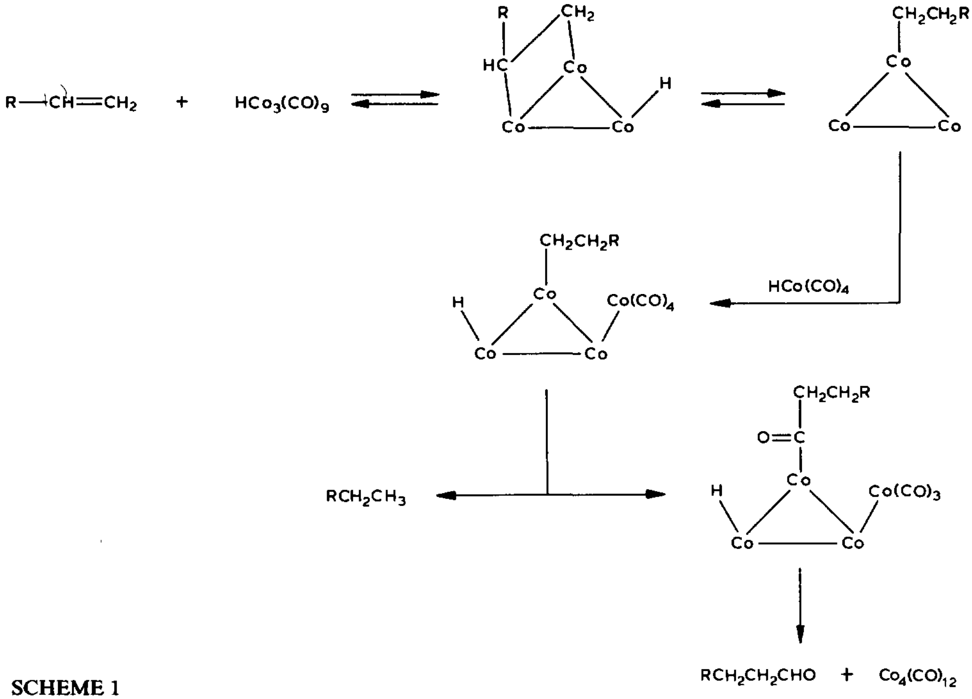
In a typical experiment $HCo_3(CO)_9$ (3.2×10^{-4} mol) and 3,3-dimethylbutene (2.8×10^{-2} mol) were mixed at −80°C under argon, then 10 ml of a n-hexane solution of $DCo(CO)_4$ (2.15×10^{-3} mol) (prepared by adding anhydrous DCl to a suspension of solvent free $LiCo(CO)_4$ in n-hexane, followed by distillation and titration) were added to the mixture and the temperature was allowed to rise to about −15°C. At this temperature the mixture rapidly became dark. After a few minutes at −15°C, the reaction was quenched by addition of an excess triphenylphosphine. One equivalent of n-heptanal (3.2×10^{-4} mol) was added as an internal standard and the reaction mixture was analyzed as described above: 4,4-dimethylpentanal (77% yield with respect to $HCo_3(CO)_9$), 70% monodeuterated (almost wholly $C_6H_{13}CDO$), 25% dideuterated, and 5% unlabeled, was formed as the main organic product along with 2,2-dimethylbutane (less than 1% with respect to residual olefin). The yield of aldehyde was not increased by use of longer reaction times at −15°C. The deuterium distribution in the aldehyde remained substantially unchanged when $DCo(CO)_4/HCo_3(CO)_9$ ratios of 3, 6.7, or 10 were used. Parallel experiments were carried out in the presence of $DCo(CO)_4$ or $HCo(CO)_4$ alone: no aldehyde was formed after 1 h at −15°C.

Results and discussion

Reaction of 3,3-dimethylbutene with $HCo_3(CO)_9$ in the presence of an excess of $HCo(CO)_4$ gave 4,4-dimethylpentanal in 77% yield (eq. 2) within a few minutes at −15°C, along with minor amounts of the hydrogenation product, 2,2-dimethylbutane. No additional aldehyde was formed on standing, and under similar conditions $HCo(CO)_4$ alone was found inactive.

$$HCo(CO)_4 + HCo_3(CO)_9 + (CH_3)_3CCH{=}CH_2 \rightarrow Co_4(CO)_{12} + (CH_3)_3CCH_2CH_2CHO \qquad (2)$$

Deuterium-labeling experiments allowed us to clarify the specific and distinct roles of $HCo(CO)_4$ and $HCo_3(CO)_9$. Fast deuterium exchange between $DCo(CO)_4$ and $HCo_3(CO)_9$ occurs at −15°C in n-hexane solution. However, the addition of neat olefin to solid $HCo_3(CO)_9$ at −80°C, followed by addition of $DCo(CO)_4$ in hexane and warming at −15°C, gave predominantly monodeuterated 4,4-dimethylpentanal, irrespective of the molar excess of $DCo(CO)_4$ used, with deuterium labeling almost exclusively at the formyl group (eq. 3).



SCHEME 1

$$DCo(CO)_4 + HCo_3(CO)_9 + (CH_3)_3CCH{=}CH_2 \rightarrow Co_4(CO)_{12} + (CH_3)_3CCH_2CH_2CDO \quad (3)$$

Apparently the rate of the H/D scrambling between $DCo(CO)_4$ and $HCo_3(CO)_9$ is considerably lowered in the presence of olefin, presumably because of a faster reaction of $HCo_3(CO)_9$ with the olefin. These experiments indicate that both I and III are involved in the observed hydroformylation, and that they play distinct roles. If the olefin to aldehyde conversion can be formally separated in the two elementary steps of hydrogen and formyl transfer to the double bond, III seems to be essentially responsible for the first and I for the second step. The Scheme illustrates a possible sequence which accounts for the experimental results. It remains to be ascertained whether III can also act as an active intermediate in reactions which occur in systems containing I and II.

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References

1 G. Fachinetti, L. Balocchi, F. Secco, M. Venturini, Angew. Chem., 93 (1981) 215; Angew. Chem. Int. Ed. Engl., 20 (1981) 204.

2 G. Fachinetti and A. Stefani, Angew. Chem., 94 (1982) 937; Angew. Chem. Suppl., (1982) 1967.