Isolation and Direct Observation of Intramolecular Hydroacylation of a *cis*-Hydridopent-4-enoylrhodium(III) Complex

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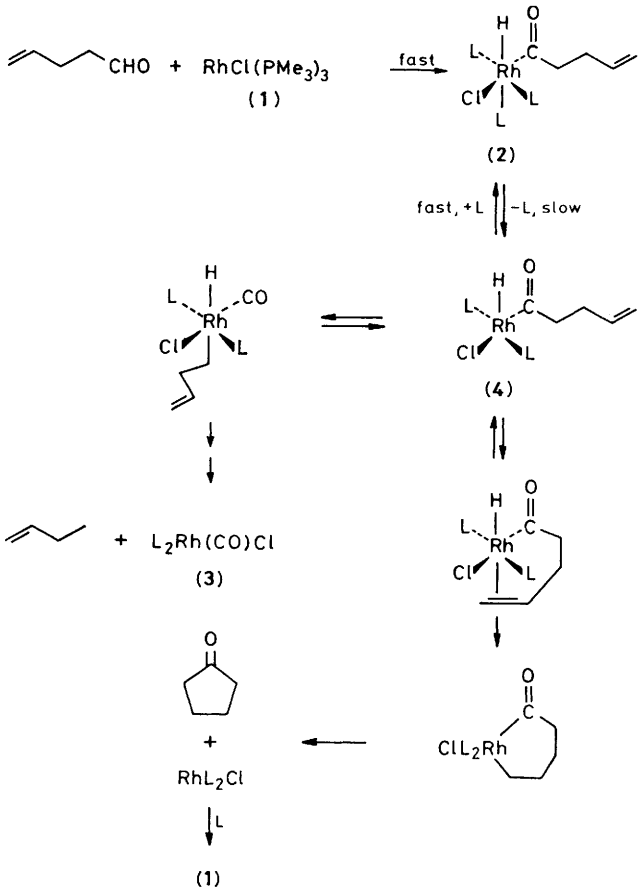
A stable *cis*-hydridopentenoylrhodium(III) trimethylphosphine complex, isolated from oxidative addition of pent-4-enal to $RhCl(PMe_3)_3$, undergoes intramolecular hydroacylation to cyclopentanone.

Rhodium-catalysed aldehyde hydroacylation of olefins,[1–4] although still in its initial development stages, is a useful method, especially the intramolecular version, for synthesis of cyclopentanones.[1–3] Attempts to isolate a postulated key intermediate, a pent-4-enoylhydridorhodium complex, have failed hitherto.[1] We now report the isolation of such an intermediate and the direct observation of its intramolecular cyclization.

Following our recent observation that *cis*-hydridoalkylrhodium(III) trimethylphosphine complexes are relatively stable owing to the very slow rate of PMe_3 dissociation from them,[5] we have studied the reaction of $RhCl(PMe_3)_3$[6] (**1**) with pent-4-enal. Addition of excess of pent-4-enal to an orange solution of (**1**) in toluene at 25 °C under N_2 resulted in a colour change to yellow after 30 min. Removal of the solvent under high vacuum and crystallization of the residue from toluene–pentane at −40 °C afforded the complex (**2**) as light yellow crystals [81% yield, i.r. (Nujol) 1940 (s, ν_{Rh-H}) and 1625 cm^{-1} (s, $\nu_{C=O}$); ^1H n.m.r. (C_6D_6) δ 1.23 (d, *J* 7.1 Hz, 9 H, PMe_3), 1.32 (t, *J* 3.0 Hz, 18 H, 2 PMe_3), 2.32 (superimposed dt, J_1 7.1, J_2 7.2 Hz, 2 H, $=CH-CH_2$), 2.79 (t, *J* 7.2 Hz, 2 H, CH_2CO), 5.00 (d, *J* 9.9 Hz, 1 H, HCH=), 5.10 (d, *J* 17.7 Hz, 1 H, HCH=), 5.95 (m, 1 H, =CH–), and −8.26 (ddt, $J_{H-P,trans}$ 189.3, J_{H-Rh} 18.3, $J_{H-P,cis}$ 14.8 Hz); $^{31}P\{^1H\}$ n.m.r. (C_6D_6) δ −6.89 (dd, J_{P-Rh} 114.3, J_{P-P} 31.3 Hz, 2 P), and −23.74 p.p.m. (dt, J_{P-Rh} 93.2, J_{P-P} 31.2 Hz, 1P)]. Since the ^1H and ^{31}P n.m.r. spectra are consistent only with a structure containing a PMe_3 ligand *trans* to the hydride ligand and having two identical *trans* PMe_3 ligands, the hydrido and acyl ligands have to be in mutually *cis* positions, as shown in structure (**2**).

Although stable at room temperature, complex (**2**) undergoes complete decomposition at 50 °C ($t_{\frac{1}{2}}$ *ca.* 1 h), resulting in intramolecular hydroacylation to form cyclopentanone (72% yield) and (**1**) (71%), in addition to a competing migra-



Scheme 1. L = PMe_3.

tory elimination process which yields $RhCl(CO)(PMe_3)_2$ (**3**) (27%), but-1-ene (27%), and PMe_3 (25%). Since (**1**) is being regenerated, this process completes a catalytic cycle for pent-4-enal intramolecular hydroacylation. Indeed, heating pent-4-enal with a catalytic amount of (**1**) at 50 °C for 2 h affords cyclopentanone (300% yield based on Rh) and but-1-ene (40%). Although Rh-promoted cyclization of pent-4-enal to cyclopentanone is well known,[1–3] catalytic activity was observed before only in the presence of ethylene.

In order to provide for double bond co-ordination, PMe_3 dissociation from (**2**) is expected. To test this, and to determine which ligand dissociates, (**2**) was partially decomposed (40 °C; 1 h) in the presence of excess of $P(CD_3)_3$.† The ^1H n.m.r. doublet at δ 1.23 completely disappeared in recovered (**2**), whereas the triplet at δ 1.32 was not affected. Thus, reversible dissociation of the PMe_3 ligand *trans* to the hydride ligand takes place, whereas the PMe_3 ligands *cis* to the hydride do not dissociate. This is probably a result of the relatively large *trans* effect exerted by the hydride ligand.

Based on these observations, a plausible mechanism for pent-4-enal intramolecular hydroacylation includes fast oxidative addition of pent-4-enal to (**1**) to yield complex (**2**), followed by slow, reversible PMe_3 dissociation from (**2**) to form a common unsaturated square-pyramidal intermediate (**4**). A trigonal bipyramidal intermediate is less likely than (**4**) because Berry pseudorotations in such a complex may lead to $P(CD_3)_3$ incoporation in positions *cis* to the hydride as well. Intramolecular insertion into the Rh–H bond of (**4**) followed by reductive elimination leads to cyclopentanone, whereas competing migratory elimination leads to the decarbonylation products (**3**) and but-1-ene (Scheme 1).

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† Prepared from CD_3MgI and $P(OPh)_3$.

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