

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

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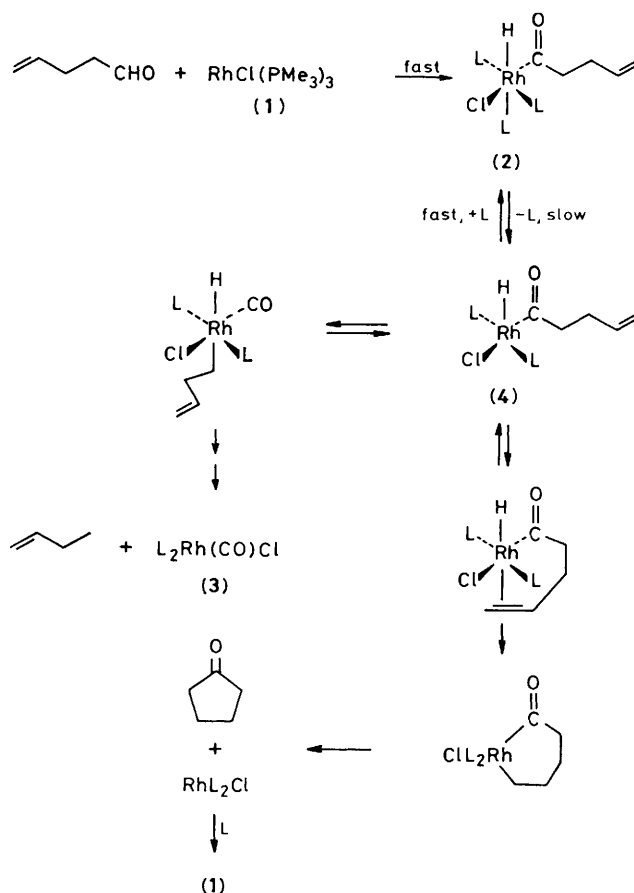
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A stable *cis*-hydridopentenoylrhodium(III) trimethylphosphine complex, isolated from oxidative addition of pent-4-enal to $\text{RhCl}(\text{PMe}_3)_3$, undergoes intramolecular hydroacylation to cyclopentanone.

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 $\text{RhCl}(\text{PMe}_3)_3$ (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, $\nu_{\text{Rh-H}}$) and 1625 cm^{-1} (s, $\nu_{\text{C=O}}$); ^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-CH₂), 2.79 (t, J 7.2 Hz, 2 H, CH₂CO), 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, $J_{\text{H-P trans}}$ 189.3, $J_{\text{H-Rh}}$ 18.3, $J_{\text{H-P cis}}$ 14.8 Hz); $^{31}\text{P}\{^1\text{H}\}$ n.m.r. (C_6D_6) δ -6.89 (dd, $J_{\text{P-Rh}}$ 114.3, $J_{\text{P-P}}$ 31.3 Hz, 2 P), and -23.74 p.p.m. (dt, $J_{\text{P-Rh}}$ 93.2, $J_{\text{P-P}}$ 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 ($t_{1/2}$ 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 $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ (**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 $\text{P}(\text{CD}_3)_3$.† 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 $\text{P}(\text{CD}_3)_3$ incorporation 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 $\text{P}(\text{OPh})_3$.