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Preliminary communication

Homogeneous decarbonylation of ethyl formate at rhodium. Evidence for the formation of a *cis*-hydride(ethoxycarbonyl) intermediate through C–H bond cleavage

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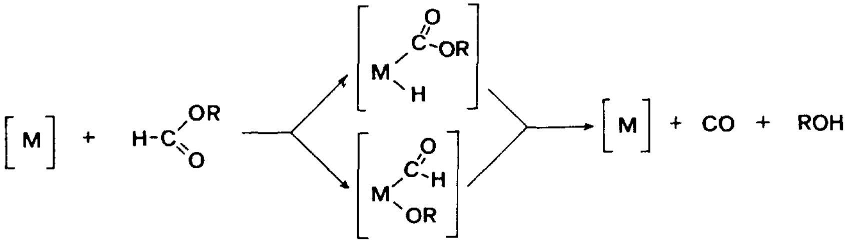
Abstract

The 16-electron fragment $[(NP_3)Rh]^+$ inserts into the sp^2 C–H bond of ethyl formate to give the octahedral complex cation $[(NP_3)Rh(H)(CO_2Et)]^+$ which can be isolated in the solid state as $SO_3CF_3^-$ salt. Thermal decomposition of the *cis*-hydride(ethoxycarbonyl) complex in benzene gives EtOH and the carbonyl $[(NP_3)RhCO](SO_3CF_3)$ ($NP_3 = N(CH_2CH_2PPh_2)_3$).

The organometallic chemistry of formate esters attracts much attention because of their central role in several metal-assisted catalytic processes, such as their transformations into CO and ROH [1] or into RH and CO_2 [2]. It is generally agreed that the homogeneous decarbonylation of HCO_2R proceeds by oxidative addition to the metal of either C–H or C–OR bonds [3] (eq. 1). In no case, however, has it proved possible to detect an intermediate sufficiently stable to isolate or study spectroscopically.



(1)

We now demonstrate that the 16-electron $[(NP_3)Rh]^+$ system can decarbonylate ethyl formate to CO and ethanol via a *cis*-hydride(ethoxycarbonyl) intermediate.

Methylation by $MeOSO_2CF_3$ of the trigonal-bipyramidal (TBP) hydride $[(NP_3)RhH]$ [4,5] in THF results in reductive elimination of methane and formation

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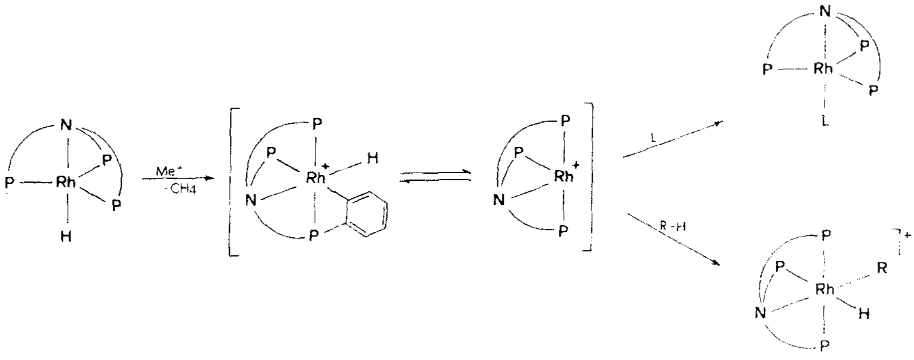
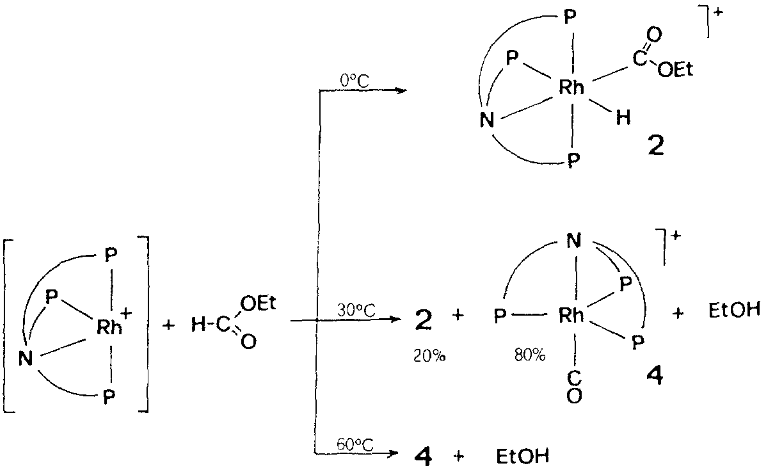


(2)

of the *o*-metalated hydride $[\{(Ph_2PCH_2CH_2)_2N(CH_2CH_2PPhC_6H_4)\}RhH]^+$ (**1**), which can be isolated in the solid state as its salt with $SO_3CF_3^-$ or BPh_4^-. The complex cation **2** is in equilibrium with the butterfly-shaped $[(NP_3)Rh]^+$ fragment, the equilibrium being shifted toward the latter by reaction with monofunctional ligands which restore the original TBP geometry around rhodium [4,5] or with substrates bearing activated C–H bonds. These oxidatively add to the $[(NP_3)Rh]^+$ system to yield octahedral (OCT) rhodium(III) derivatives [4,5] (eq. 2, where L = halides, pseudohalides, H^-, CO and R = C≡CR′, COR′, Ph).

A THF solution of the *o*-metalated hydride, prepared as shown in eq. 2, reacts with a threefold excess of ethyl formate in a fashion which is strictly dependent on the temperature. At 0 °C, a slow reaction takes place to give after 3 h a quantitative yield of the rhodium(III) OCT *cis*-hydride(ethoxycarbonyl) complex, $[(NP_3)RhH(CO_2Et)](SO_3CF_3)$ (**2**), as colourless microcrystals [$^{31}P\{^1H\}$ NMR (C_6D_6, 0 °C): AM_2X spin system, 39.60 ppm, dd, $J(P_MRh)$ 116.0 Hz, $J(P_MP_A)$ 20.6 Hz, 20.05 ppm, dt, $J(P_ARh)$ 116.0 Hz. ^1H NMR (C_6D_6, 0 °C): δ 3.95, OCH_2CH_3, q, $J(HH)$



(3)

12.5 Hz, δ 1.24, OCH_2CH_3, t; δ −7.36 ppm, Rh–H, dm, $J(HP_{trans})$ 151.8, $J(HP_{cis})$ 8.3, J(HRh) 15.8 Hz. IR (Nujol mulls): 1715(s), ν(C=O), 1940(m), ν(Rh–H)].

At 30 ° C, the reaction gives a mixture of ethanol, complex cation **2**, and the known TBP rhodium(I) complex $[(NP_3)RhCO](SO_3CF_3)$ (**4**) [4]. At 60 ° C, only the carbonyl complex **3** and ethanol are obtained (eq. 3). In good agreement with these findings when a solution of a pure sample of **2** in benzene is kept at 60 ° C there is a ready quantitative decomposition to **3** and EtOH.

Another rhodium system of the type L_4M-d_8 able to decarbonylate HCO_2Et under very mild conditions is the $[(PP_3)Rh]^+$ fragment. This is generated in THF by CH_4 reductive elimination from the unstable *cis*-hydride(methyl) complex $[(PP_3)RhH(Me)]^+$ ($PP_3 = P(CH_2CH_2PPh_2)_3$) [6]. In contrast with the results obtained with the NP_3 complex, no *cis*-hydride(ethoxycarbonyl) intermediate could be detected, and the carbonyl cation $[(PR_3)RhCO]^+$ and EtOH were the only products regardless of the temperature. Since introduction of phosphorus in place of nitrogen can substantially modify the frontier orbitals of the metal fragment [7], it is possible that the decarbonylation reaction of HCO_2Et proceeds by an alternative pathway. Theoretical studies are under way to try to rationalize the differing behaviour patterns of the $[(NP_3)Rh]^+$ and $[(PP_3)Rh]^+$ systems.

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