

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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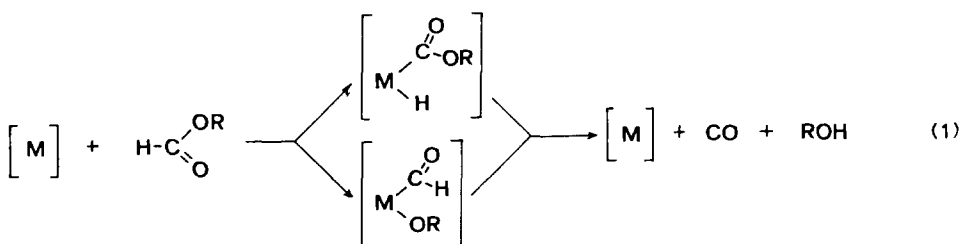
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Abstract

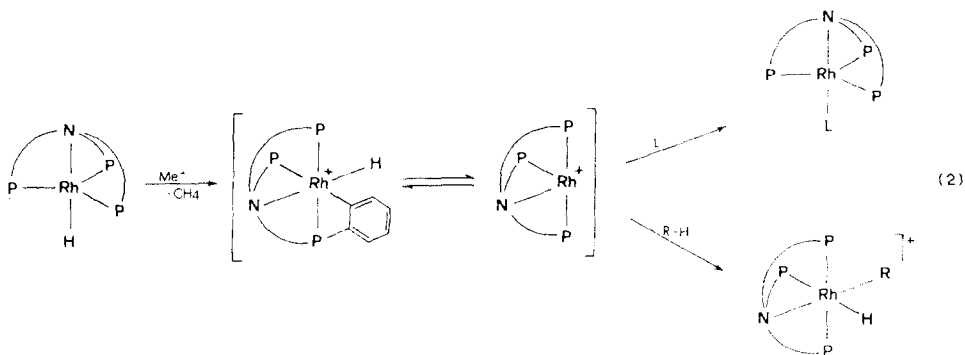
The 16-electron fragment $[(NP_3)Rh]^+$ inserts into the sp^2 C–H bond of ethyl formate to give the octahedral complex cation $[(NP_3)Rh(H)(CO_2Et)]^+$ which can be isolated in the solid state as $SO_3CF_3^-$ salt. Thermal decomposition of the *cis*-hydride(ethoxycarbonyl) complex in benzene gives EtOH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



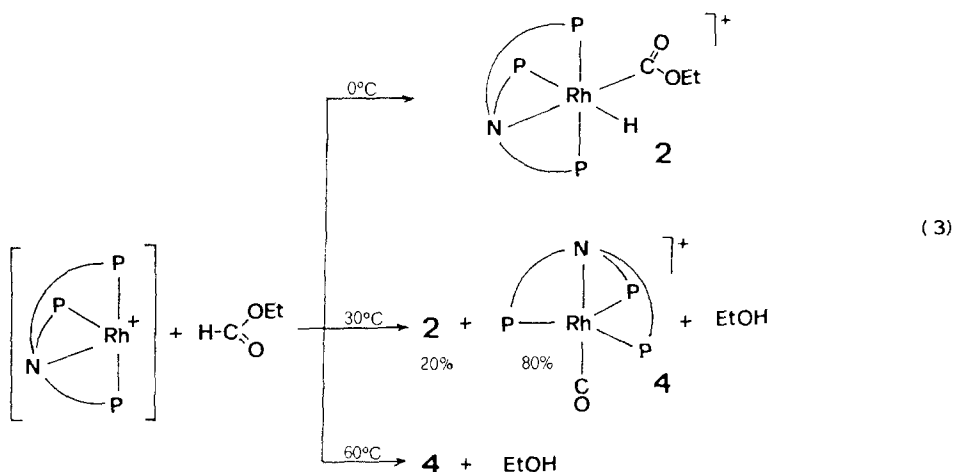
We now demonstrate that the 16-electron $[(NP_3)Rh]^+$ system can decarbonylate ethyl formate to CO and ethanol via a *cis*-hydride(ethoxycarbonyl) intermediate.

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



of the *o*-metalated hydride $[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2\text{PPhC}_6\text{H}_4)\text{RhH}]^+$ (**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 $[(\text{NP}_3)\text{Rh}]^+$ 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 $[(\text{NP}_3)\text{Rh}]^+$ system to yield octahedral (OCT) rhodium(III) derivatives [4,5] (eq. 2, where L = halides, pseudohalides, H^- , CO and R = $\text{C}\equiv\text{CR}'$, 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, $[(\text{NP}_3)\text{RhH}(\text{CO}_2\text{Et})](\text{SO}_3\text{CF}_3)$ (**2**), as colourless microcrystals [$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 0°C): AM_2X spin system, 39.60 ppm, dd, $J(\text{P}_\text{M}\text{Rh})$ 116.0 Hz, $J(\text{P}_\text{M}\text{P}_\text{A})$ 20.6 Hz, 20.05 ppm, dt, $J(\text{P}_\text{A}\text{Rh})$ 116.0 Hz. ^1H NMR (C_6D_6 , 0°C): δ 3.95, OCH_2CH_3 , q, $J(\text{HH})$



12.5 Hz, δ 1.24, OCH_2CH_3 , t; δ -7.36 ppm, Rh-H, dm, $J(\text{HP}_{\text{trans}})$ 151.8, $J(\text{HP}_{\text{cis}})$ 8.3, $J(\text{HRh})$ 15.8 Hz. IR (Nujol mulls): 1715(s), $\nu(\text{C}=\text{O})$, 1940(m), $\nu(\text{Rh}-\text{H})$.

At 30 °C, the reaction gives a mixture of ethanol, complex cation **2**, and the known TBP rhodium(I) complex $[(\text{NP}_3)\text{RhCO}](\text{SO}_3\text{CF}_3)$ (**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 $\text{L}_4\text{M}-d_8$ able to decarbonylate HCO_2Et under very mild conditions is the $[(\text{PP}_3)\text{Rh}]^+$ fragment. This is generated in THF by CH_4 reductive elimination from the unstable *cis*-hydride(methyl) complex $[(\text{PP}_3)\text{RhH}(\text{Me})]^+$ ($\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$) [6]. In contrast with the results obtained with the NP_3 complex, no *cis*-hydride(ethoxycarbonyl) intermediate could be detected, and the carbonyl cation $[(\text{PR}_3)\text{RhCO}]^+$ 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 $[(\text{NP}_3)\text{Rh}]^+$ and $[(\text{PP}_3)\text{Rh}]^+$ systems.

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