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Preliminary communication

HYDRIDO CYCLOPENTADIENYLIRON DICARBONYL AND ITS ROLE IN OLEFIN HYDROFORMYLATION

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Summary

The compound hydrido cyclopentadienyliron dicarbonyl has been shown by infrared and proton NMR to be present in substantial quantities during hydroformylation of propene and 1-pentene in the presence of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. This and related observations strongly suggest that the hydride is an important link in the catalytic cycle as is $HCo(CO)_4$ in $Co_2(CO)_8$-catalyzed olefin hydroformylation.

Recently Baird and co-workers have presented compelling evidence that hydrido cyclopentadienyliron dicarbonyl, $CpFe(CO)_2H$ ($Cp = \eta^5\text{-}C_5H_5$), is considerably more stable with respect to decomposition to $[CpFe(CO)_2]_2$ than was previously believed [1]. The dimeric complex has been reported by two separate groups [2—4] to homogeneously catalyze olefin hydroformylation. By analogy to the well-known $Co_2(CO)_8$ system [5] it seems logical to presume that $CpFe(CO)_2H$ is an important component of the catalytic cycle and that it is formed as shown below.

$$[CpFe(CO)_2]_2 + H_2 \rightleftharpoons 2CpFe(CO)_2H \qquad (1)$$

This was in fact suggested in the original work [2] but no supporting evidence was presented. More recently Ugo and co-workers described high pressure IR data and concluded that: "even at 50—60 atm of hydrogen pressure, the amount of hydride formed in situ is rather low" [3]. We present herein our preliminary findings for this system which demonstrate both the unequivocal presence of $CpFe(CO)_2H$ and its stability under conditions typical of the hydroformylation process.

Consistent with the results reported earlier by Tsuji [2] and Ugo [3,4] we

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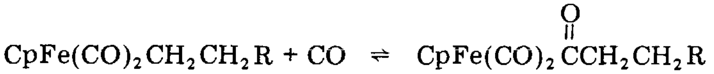
find that $[CpFe(CO)_2]_2$ in toluene solvent hydroformylates propene and 1-pentene at 100—150°C and 1000—2000 psi syngas pressure (1/1 CO/H_2) to mixtures of branched and linear aldehydes. Infrared spectra of solutions taken from the reaction mixture either during reaction or after cooling to room temperature showed a strong sharp band at 2015 cm^{-1} in addition to the characteristic bands due to the dimer at 2001, 1958 and 1790 cm^{-1}. The bands expected [6] for $CpFe(CO)_2H$ are 2014 and 1960 cm^{-1} but the latter would be obscured by the 1958 absorption of the dimer. The presence of the hydride was demonstrated unequivocally by the proton NMR spectrum of the mixture which showed C_5H_5 and Fe—H resonances at 5.24 and —11.62 ppm respectively relative to TMS (lit. [6] 5.26, —11.91). Similar results were obtained with H_2 and CO/H_2 atmospheres in the absence of olefin, ruling out hydride formation due to an olefin/dimer reaction. The proportions of hydride and dimer in the reaction mixtures are unchanged over periods of up to two weeks at room temperature on the basis of carbonyl absorption intensities in the IR spectra. This is in agreement with the findings of Baird [1].

Information regarding the extent of reaction 1 was obtained from infrared spectra of typical reaction mixtures. By comparison of spectra with those of known mixtures of the hydride and dimer, we estimate that 35±10% of the dimer is converted to the hydride under hydroformylation conditions or by hydrogen alone at 100—150°C. High pressure IR studies of the mixture under reaction conditions are required for more precise definition of the position of equilibrium 1.

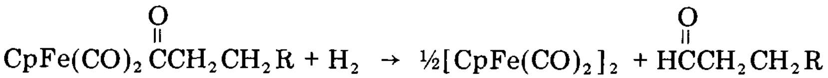
Assuming that hydride formation is the primary entry to the catalytic cycle, subsequent steps for the eventual production of aldehyde could logically proceed as follows [2—5]:

$$CpFe(CO)_2H + RCH{=}CH_2 \rightleftharpoons \begin{array}{l} CpFe(CO)_2CH_2CH_2R \\ (CpFe(CO)_2CHRCH_3) \end{array} \qquad (2)$$



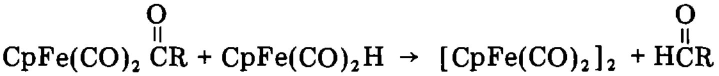
$$CpFe(CO)_2CH_2CH_2R + CO \rightleftharpoons CpFe(CO)_2\overset{O}{\overset{\|}{C}}CH_2CH_2R \qquad (3)$$

Reactions of $CpFe(CO)_2H$ with activated olefins [1,7,8] and butadiene [9] (eq. 2) are in fact quite rapid. King [10] has shown that $CpFe(CO)_2C_2H_5$ is completely converted to $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_2H_5$ under 325 atm CO at 97°C (cf. eq. 3). Subsequent steps leading to aldehyde formation remain unclear. Direct reaction of an iron acyl with hydrogen (eq. 4) led to dimer formation, but no aldehyde was observed [10]. A bimolecular reaction between iron acyl and hydride (eq. 5) is attractive based on recent examples for a variety of metals [11]. We find however, that $CpFe(CO)_2\overset{O}{\overset{\|}{C}}CH_3$ and $CpFe(CO)_2H$ do not react



$$CpFe(CO)_2\overset{O}{\overset{\|}{C}}CH_2CH_2R + H_2 \rightarrow \tfrac{1}{2}[CpFe(CO)_2]_2 + H\overset{O}{\overset{\|}{C}}CH_2CH_2R \qquad (4)$$

at 25—90°C to give detectable quantities of acetaldehyde, although the iron dimer is produced in small amounts.



$$\mathrm{CpFe(CO)_2\overset{\overset{O}{\|}}{C}R + CpFe(CO)_2H \rightarrow [CpFe(CO)_2]_2 + H\overset{\overset{O}{\|}}{C}R} \qquad (5)$$

At 130—140°C acetaldehyde is formed, but in amounts apparently smaller than reacted acetyl and hydride. The latter observation could be due to secondary reactions of the aldehyde to give as yet undetected products. Experiments with acyls leading to more tractable aldehyde products (i.e. $R = C_3H_7$, eq. 5) and at various CO/H_2 ratios are in progress. At present we favor eq. 5 as the aldehyde forming step, but further work is required before the mechanism of hydroformylation with this catalyst system is completely understood*.

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*One of the reviewers has suggested that an additional source of iron hydride in eq. 5 could be β-elimination from the iron alkyl formed earlier in the cycle (reverse of eq. 2). We plan to examine this possibility as well as other yet unresolved questions and will report our findings in a full paper.