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Preliminary communication

METAL CLUSTER CATALYSIS

III*. SELECTIVE HOMOGENEOUS HYDROGENATIONS CATALYZED BY $[(\eta^5\text{-}C_5H_5)Fe(\mu_3\text{-}CO)]_4$

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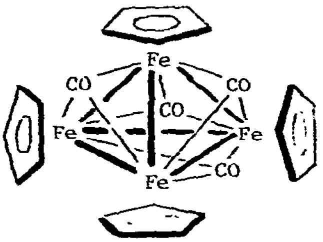
Summary

The iron cluster, $[(\eta^5\text{-}C_5H_5)Fe(\mu_3\text{-}CO)]_4$, 1, catalyzes the selective hydrogenation of alkynes to alkenes at 100–130° and 100–1000 psig and the selective reduction of terminal alkynes to olefins in the presence of alkenes or internal alkynes. Internal alkynes are slowly reduced to cis olefins, aryl nitro groups to aniline derivatives, and terminal activated carbon-carbon double bonds (methyl acrylate, acrylonitrile) are hydrogenated. The cluster concentration, monitored by high pressure liquid chromatography, was unchanged after 1148 and 1410 turnovers. Cluster 1 was isolated in 95–97% yields after catalytic reduction (1000 turnovers) and no other iron-containing species were detected. After 280 turnovers, the catalyst solution was filtered through an ultrafiltration membrane into a second vessel where hydrogenation of 1-pentyne continued. Fragmentation of 1 to

$(\eta^5-C_5H_5)Fe(CO)_2H$ appears to be ruled out since $[(\eta^5-C_5H_5)Fe(CO)_2]_2$, which gives this iron hydride when heated in hydrogen, was not active in 1-pentyne reductions. Thus cluster $\underset{\sim}{1}$ appears to be the third example of a first row cluster catalyst which resists fragmentation due to bridging ligands in addition to metal-metal bonding.

The use of soluble transition metal cluster compounds as catalysts has been an area of intense research interest [1,2] as possible models for catalysis at metal surfaces [2]. Despite intense studies of the bonding of small molecules to clusters and fluxional behavior of clusters [3], only a modest number of reports document reactions where clusters seem to be the true catalysts [1]. Examples include the reduction of carbon monoxide in the presence of $Ir_4(CO)_{12}$ [4] and the formation of ethylene glycol from synthesis gas catalyzed by rhodium cluster anions [5]. While the hydrogenation of olefins and alkynes by homogeneous mononculear complexes is widely practiced [6], clusters have received relatively little attention in this regard [7]. Activated olefins were reduced with carbon monoxide and water in the presence of $Rh_6(CO)_{16}$ [8] and styrene is hydrogenated in the presence of $Co_4(CO)_{12}$, $Co_3Rh(CO)_{12}$, and $Co_2Rh_2(CO)_{12}$ [9].

A key problem associated with the use of clusters in catalysis is their propensity to fragment into homonuclear moieties under reaction conditions [2a-c]. $Co_2(CO)_8$ [10] and $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ [11, 12] fragment during hydroformylation reactions. One approach to avoid fragmentation is the use of third row clusters which have stronger metal-metal bonds. We have advocated and pioneered the use of first row clusters that are bound together both by metal-metal bonds and by stable, nonfluxional, bridging ligands [1, 2a, 2c]. Indeed, we report here the selective hydrogenation of alkynes, activated olefins, and nitro groups catalyzed by $[(\eta^5-C_5H_5)Fe(\mu_3-CO)]_4$ [13], $\underset{\sim}{1}$. In cluster $\underset{\sim}{1}$ each iron atom is bonded to a) three other irons and b) three triply-bridging carbonyl ligands. In each case, **1** was recovered in 95-97% yields from the reaction solutions after long reaction periods and molar turnovers in excess of 1000. Isolation and tlc analysis revealed no other iron containing compounds.



1

$$C_3H_7C\equiv CH \xrightarrow[\substack{H_2(100\text{-}1000\ psi)\\ 100\text{-}130°}]{\mathbf{1}} C_3H_7CH{=}CH_2$$

The hydrogenation of 1-pentyne to 1-pentene was readily catalyzed by **1** at 100-140° using hydrogen pressures from 100 to 1000 psi. The cluster was first dried by heating at 80° and 0.1 torr (where **1** is stable and its IR spectra is unchanged). In general, the selectivity to 1-pentene is high, and isomerization to 2-pentene is very slow. At high conversions, this selectivity decreased from ~85% to ~75% as the pressure increased from 100 to 250 psi and then remained unchanged to 1000 psi. (See Table 1). At lower conversions, selectivity was higher. At 46% conversion (120°, 100 psi), a 98% selectivity to 1-pentene was obtained which decreased to 92% at 85% conversion. At long reaction times, **1** does not promote olefin hydrogenation in contrast to the homogeneous catalysts $[Rh(NBD)(PR_3)_2]^+PF_6^-$ [6c] and $RhCl(PPh_3)_3$ [14] which effected rapid olefin hydrogenation once alkyne was exausted.

Internal alkynes are hydrogenated more slowly than terminal alkynes. A 1:1 mixture of 1-pentyne and 3-hexyne, after 11 h at 100 psi and 100°, gave a 62% conversion of 1-pentyne to 1-pentene (93.5% selectivity) and only a 4% conversion of 3-hexyne to cis-3-hexene (100% selectivity). The faster reduction of terminal alkynes contrasts shraply with the use of $[Rh(NBD)(PR_3)_2]^+PF_6^-$ [6c] which catalyzed the hydrogenation of internal alkynes more rapidly than terminal alkynes.

While catalysis by a cluster cannot be definitively proved [7], the fragmentation of **1** appears unlikely in these reductions. Not only was **1**

Table 1. Homogeneous Hydrogenations Catalyzed by $[(\eta^5\text{-}C_5H_5)Fe(\mu_3\text{-}CO)]_4$.[a]

Substrate	Temp. °C	Pressure psi	Time h	Conversion %	Products (% yield)
1-Pentyne[b]	120	100	6	85	1-pentene (73), 2-pentene (8.8), pentane (3.8)
1-Pentyne	120	105	88	99	1-pentene (84), 2-pentene (10.1), pentane (3.0)
"	120	460	46	83	1-pentene (61), 2-pentene (4.2), pentane (17)
"	120	685	120	98	1-pentene (73), 2-pentene (2.6), pentane (21.4)
"	120	980	70	62	1-pentene (48), 2-pentene (0), pentane (13.7)
2-Pentyne	120	504	40	4.4	2-pentene (4.2), pentane (0.2)
1-Pentene	130	460	57	61	2-pentene (55), pentane (6)
1,3-Cyclooctadiene	100	100	24	3.7	cyclooctane (2.9), cyclooctene (0.8)
Nitrobenzene	100	100	26	6	aniline (6)
"	130	300	24	31	aniline (31)
Methyl acrylate	100	100	24	32	Methyl propanoate (32)
Acrylonitrile	100	100	24	26	Propionitrile (26)
Ethyl crotonate	100	100	24	2.3	Ethyl butarate (2.3)
Benzonitrile	100	100	24	0	-
Methyl ethyl Ketone	100	100	24	0	-
Nitropropane	130	300	24	0	-

[a] Each reaction employed 0.05 mmol of catalyst, benzene (15 ml), substrate (20.3 mmol).

[b] Catalyst 1 was dried at 80°C, 0.1 torr. for 12h prior to reaction.

isolated in high yield after each reduction, but it is stable for long periods in boiling xylene. Also, 1 is known [15] to undergo multiple oxidations (0→+1→+2) and reduction (0→ -1) without fragmenting. Furthermore, if 1 did fragment in the presence of alkyne and hydrogen, it is difficult to imagine how it could reform species 1. The concentration of 1 was monitored during 1-pentyne hydrogenations (125°, 600 psi H_2) using high pressure liquid chromatography (HPLC). The catalyst concentration was unchanged within the limits of HPLC detection (±0.7%) after 130, 418, 1148, and 1410 turnovers. Additionally, the reaction solutions remained clear; they did not scatter light and no evidence of colloidal iron was observed. Finally, after 280 turnovers (125°, 600 psi H_2, 1-pentyne, benzene), the reaction solution was filtered through an ultrafiltration membrane into a second reaction vessel where hydrogenation continued without an induction period. These results suggest 1 functions as the active catalyst, supporting the idea that first row clusters with bridging ligands will be a fertile area for others to explore cluster catalysis.

Dienes, like olefins, resisted hydrogenation using 1. Similarly, nitriles and keto groups were inert. Nitrobenzene was only 6% converted to aniline under these conditions but at 130° and 300 psi a 31% conversion occurred in 24 h. Activated terminal olefins such as methyl acrylate and acrylonitrile were hydrogenated but internal activated olefins (ethyl crotonate) resisted reduction at 100°. 1 did not catalyze the hydrogenation of carbon monoxide, the water-gas shift reaction, hydroformylation, or alkoxycarbonylation of olefins. Further studies are underway in our laboratory.

One might suggest that 1 fragments to η^5-$C_5H_5Fe(CO)_2H$ under reaction conditions. Thus, attempts were made to hydrogenate 1-pentyne using $[\eta^5$-$C_5H_5Fe(CO)_2]_2$, which is known to generate η^5-$C_5H_5Fe(CO)_2H$ when heated with hydrogen. At temperatures from 100-120° (100-400 psi) the dimer did not catalyze reduction of 1-pentyne. Furthermore, 1 was not recovered from these reactions. Thus, in reactions catalyzed by 1, fragmentation to η^5-$C_5H_5Fe(CO)_2H$ must not occur.

A typical hydrogenation of 1-pentyne was conducted as follows. Benzene (15 ml), **1** (.030 g., 0.05 mmol), and 1-pentyne (2.0 ml, 20.3 mmol) were charged into the reaction vessel under nitrogen and the reactor (glass) was flushed three times with hydrogen. The reactor was then pressurized with hydrogen to 100 psi and placed in a preequilibrated constant temperature bath at 100°. After 6 h the reaction solution was analyzed by glc [15' x 1/8", 15% tricresylphosphate on chromosorb W (acid washed, DMCS treated, 80-100 mesh), temperature programmed 20° (6 min.), 15°/min. to 100° (hold 10 min.)]. The products were pentane (3.8%), 1-pentene (73.0%), trans-2-pentene (8.8%), 2-pentyne (1.6%), and 1-pentyne (14.7%).

Acknowledgements

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