Novel Conversion of Ethylene into Ethane and Buta-1,3-diene Catalysed by Titanium Metallocenes

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Summary The compounds μ-($\eta^1:\eta^5$-cyclopentadienyl)-tris-(η-cyclopentadienyl)dititanium(*Ti–Ti*) (**1**) and μ-($\eta^5:\eta^5$-fulvalene)di-μ-hydrido-bis(η-cyclopentadienyltitanium) (**2**) have been found to be homogeneous catalysts for the conversion of ethylene into ethane and buta-1,3-diene.

Mixtures of titanium compounds and organoaluminium compounds (Zeigler–Natta catalysts) have been widely employed for the oligomerization and polymerization of olefins. However, little is known as to the reactivity of discrete titanium compounds with olefins. We have shown that $[(\eta\text{-}C_5H_5)_2\overline{Ti\text{-}\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4)\text{-}Ti}(\eta\text{-}C_5H_5)]$ (**1**)[1] and $[\mu\text{-}(\eta^5:\eta^5\text{-}C_{10}H_8)\text{-}\mu\text{-}(H)_2\text{-}(\eta\text{-}C_5H_5)_2Ti_2]$ (**2**)[2–4] catalyse some olefin hydrogenation and isomerization reactions.[5] We have now found that (**1**) and (**2**) are catalysts for the conversion of ethylene into ethane and buta-1,3-diene [reaction (1)]. As far as we are aware, this is a novel reaction, although some related transformations have been reported. Specifically, mixtures of ethylene and benzene, when passed over heated Re, Mo, or W oxides, are said to yield buta-1,3-diene; ethylene alone however, does not give the diene.[6] Certain iridium phosphine hydride complexes are reported to catalyse the disproportionation of hex-1-ene into hexane and hexadienes.[7]

$$3C_2H_4 \rightarrow C_2H_6 + CH_2{=}CH\text{–}CH{=}CH_2 \qquad (1)$$

Reaction (1) was performed by treating solutions of (**1**) or (**2**) in toluene or tetrahydrofuran (THF) with ethylene (8—70 atm, 23—160 °C). It is important to note that (**1**) and (**2**) are highly air sensitive; these catalysts and the accompanying reagents were handled with the rigorous exclusion of oxygen, using techniques described earlier.[1,5] Experimental conditions and product yields are summarized in the Table.

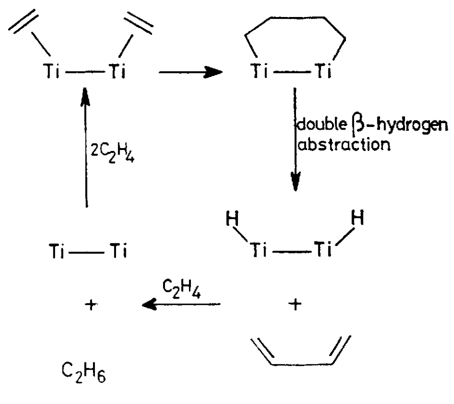
In a very slow reaction, ethylene over (**1**) or (**2**) yields ethane, buta-1,3-diene, butenes, and traces of n-butane. The yield of buta-1,3-diene is favoured by high pressures of ethylene. Prior addition of but-1-ene (36 mol/mol of catalyst) does not significantly improve the yield of the diene. The best selectivity towards buta-1,3-diene is achieved when THF (a co-ordinating solvent) is used. However, other potential ligands, when added to the system, either lower the yield of the diene (triphenylphosphine) or totally quench the reaction (triphenyl phosphite or 2,2′-bipyridine). In most reactions more ethane is formed than buta-1,3-diene. We attribute this to a loss of the diene by the formation of involatile oligomers, as well as by a possible H-transfer from the cyclopentadienyl ligands of the catalyst. In run 3 (Table), the increase in weight due to the formation of oligomers (remaining after exhaustive washing with octane and vacuum drying) accounts for *ca.* 60% of this 'excess' ethane. When the reaction was done using a mixture of THF and [$^2H_8$]THF, no incorporation of deuterium in the products was noted. This rules out the possibility of any H-transfer reactions from the solvent.

Catalyst (**1**) works best at room temperature. Heating accelerates the reaction, but there is an accompanying loss of free buta-1,3-diene (see run 5). Solutions of (**2**), though feebly active at room temperature, give the best yields of the diene at *ca.* 100 °C. In the course of reaction with ethylene at *ca.* 100 °C, (**2**) changes to a brown compound which does not have the intense absorption at 1230 cm^{-1} (ν_{M-H}) of the parent hydride. Presumably the hydride ligands in (**2**) react with ethylene to give the reaction catalyst (and ethane).

TABLE. Reactions of ethylene in the presence of $[(C_5H_4)(C_5H_5)_3Ti_2]$ (**1**) and $[(C_{10}H_8)(C_5H_5)_2Ti_2H_2]$ (**2**)[a]

Run no.	Catalyst	Solvent	Catalyst conc./ $M \times 10^2$	Ethylene pressure/ atm	Temp./ °C	Time/ days	Product[d] (Turnover no.) (Mol product/mol of catalyst)			
							Ethane	Buta-1,3-diene	But-1-ene	2-Butenes
1	(**1**)[b]	PhMe	4·33	66	23	9	2·3	1·9	3·2	<0·3
2	(**1**)[b]	THF	4·70	59	"	9	7·6	7·4	2·7	"
3	(**1**)[c]	$[^2H_8]$THF[f]	3·23	12	"	10	7·5[e]	1·4[e]	0·6[e]	"
4	(**1**)[c]	THF	3·33	59	"	11	11	7·3	3·8	"
5	(**1**)[c]	"	3·33	39	90	0·87	5·8	1·6	1·0	"
6	(**1**)[b]	"	4·69	12	23	10	4·3	2·5	0·4	—
7	(**2**)	"	4·69	12	"	10	—	0·5	—	—
8	(**2**)	PhMe	3·52	11	98	2·5	12	3·3	0·6	0·5
9	(**2**)	THF	4·68	39	102	3·25	59	22	1·6	<0·3
10	(**2**)	"	4·69	11	151	1·0	18	0·6	0·3	2·4

[a] The hydride (**2**) was prepared by reduction of $[(C_5H_5)_2TiCl_2]$ with sodium–naphthalene at 23 °C in THF (refs. 2 and 3). The crude light green product was purified by washing with small amounts of toluene and freed from residues of (**1**) by treatment with hex-1-ene (ref. 5). [b] Crude (**1**) as obtained from reduction of $[(C_5H_5)_2TiCl_2]$ (ref. 1). [c] Crystalline $[(C_5H_4)(C_5H_5)_3Ti_2(THF)]$.THF was used as a source of very pure (**1**) (ref. 1). [d] Products were analysed by g.l.c. (n-octane on Porasil column, He-carrier, 23 °C), and mass spectral techniques. The identity of but-1,3-diene was also confirmed by its gas-phase i.r. spectrum. [e] No deuterium incorporation was observed. [f] THF : $[^2H_8]$THF = 1 : 0·7.



SCHEME

Recently, it has been suggested that metallocyclic compounds might be intermediates in reactions of 'titanocene' species with ethylene.[8] A key structural feature of (**1**) is the presence of a highly exposed and co-ordinatively unsaturated metal–metal bond.[1] It is reasonable to suppose that reaction (1) proceeds over unsaturated Ti–Ti species *via* the formation of bimetallic heterocyclic intermediates as shown in the Scheme. Currently, there is much interest in the application of metal cluster compounds as homogeneous catalysts.[9] Our reaction is one of the very few novel chemical transformations which takes place over polymetallic organometal compounds.

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