Journal of Organometallic Chemistry, 198 (1980) C65—C68

Preliminary communication

PHOTOCATALYTIC HOMOGENEOUS HYDROGENATION OF OLEFINS WITH ALKYLTITANOCENE COMPOUNDS

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(Received July 24th, 1980)

Summary

Dialkyltitanocene compounds, $(\eta^5\text{-}C_5H_5)_2TiR_2$ (R = CH_3; $CH_2C_6H_5$; C_6H_5), when photolyzed under hydrogen are efficient catalyst precursors for the hydrogenation of linear and cyclic olefins under mild conditions (25°C; 1 atm). With R = CH_3 and $CH_2C_6H_5$ hydrogenation is photocatalytic whereas with R = C_6H_5 it is photoassisted. The latter precursor selectively hydrogenates linear dienes to monoenes. These catalytic reactions are suspected to proceed by light-induced homolytic cleavage of titanium—carbon bonds. Formation of Ti^{3+} species in significant proportions was revealed by ESR.

In the field of homogeneous hydrogenation of olefins, known examples of photocatalysis have been restricted so far to reactions involving metal carbonyls as precursors [1—10]. Catalytically active species for hydrogenation generated by photocleavage of metal—carbon σ bonds do not seem to have been reported previously in spite of the extensive studies devoted to the photochemistry of the alkyl transition-metal compounds [11—15].

We now report on an efficient photocatalytic system for the homogeneous hydrogenation of olefins under mild conditions (25°C; 1 atm), using alkyltitanocene compounds, Cp_2TiR_2, as precursors (Cp = $\eta^5\text{-}C_5H_5$; I, R = CH_3, II, R = $CH_2C_6H_5$; III, R = C_6H_5 [16]. All these compounds are air-stable and are easily prepared in high yields from Cp_2TiCl_2 and the appropriate alkylating reagent.

The active catalytic species are generated by irradiation of the precursors I, II and III in solution (heptane or benzene) for a few minutes (ten to fifteen) under hydrogen with UV-visible light* prior to the introduction of the substrate. A rapid color change takes place concomitant with the formation of the hydro-

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*The light source used was a HANAU TQ-150 lamp water-cooled in a Pyrex jacket and emitting above 300 nm. Compounds I, II and III have absorption bands at 370 (ϵ = 930), 425 (ϵ = 1460) and 490 (ϵ = 750) nm, respectively. Blank experiments were done to ensure complete absence of catalytic activity without the use of light.

carbon RH (identified by GLC; with I under deuterium both CH_4 and CH_3D are formed and were detected by mass spectroscopy). The olefin is then introduced, whereupon the solution becomes completely homogeneous, and hydrogenation is usually complete within 30 minutes.

It is notable that the formation of the catalyst depends on the nature of the σ-bonded alkyl ligand in the precursor. Thus hydrogenation with I and II is truly photocatalytic in that light is needed merely to trigger the generation of the catalyst, the reaction proceeding then in the dark. With III hydrogenation is photoassisted and continuous photolysis is necessary, which suggests bond breaking upon absorption of each quantum of light.

All these catalysts show high activity in the hydrogenation of various linear and cyclic olefins and unsaturated ethers (Table 1). They are also active towards double-bond migration; for this purpose the isomerisation reaction is conducted under an inert atmosphere after generation of the catalyst under hydrogen. Thus with I and within a few minutes, hex-1-ene is converted into hex-2-ene and hex-3-ene, and cycloocta-1,5-diene into cycloocta-1,3-diene. These systems are, however, totally inactive towards olefins bearing strongly coordinating functional groups such as unsaturated amines, aldehydes, ketones and acids, a property shared with other early transition-metal catalysts.

An important feature which highlights the role played by the σ-bonded alkyl ligand is the selectivity exhibited by III in the hydrogenation of linear dienes. Monoenes are obtained almost exclusively, in contrast to hydrogenation with II and III which yields a mixture of isomers along with the saturated hydrocarbon (Table 2).

No doubt the high activity of the system described is associated with the facile photocleavage of the Ti—alkyl bond leading to reduced titanium species [15]. The difference in activity exhibited by III compared to I and II tends to in-

TABLE 1

PHOTOCATALYTIC HYDROGENATION (25°C, 1 atm.) OF OLEFINS WITH DIALKYL- AND DIARYL-TITANOCENE COMPOUNDS

Catalyst (precursor)[a]	Olefin[b]	Initial hydrogenation rate[c]	Total olefin conversion (%)	Time (min)	Products
$Cp_2Ti(CH_3)_2$ (I)	cyclohexene	125	80	60	cyclohexane
	cyclooctene	380	80	18	cyclooctane
	hex-1-ene	623	90	20	hexane (85%) + isomers
	hex-2-ene (*cis* + *trans*)	142	91	20	hexane
	styrene	—	100	3	ethylbenzene
	isobutyl vinyl ether	360	80	7	isobutyl ethyl ether
	diphenyl-acetylene (*d*)	—	100	15	diphenylethane
$Cp_2Ti(CH_2Ph)_2$ (II)	cyclohexene	68	65	30	cyclohexane
	cyclooctene	153	60	13	cyclooctane
	hex-1-ene	400	90	12	hexane (75%) + isomers
$Cp_2Ti(Ph)_2$ (III)	cyclohexene	36	50	30	cyclohexane
	cyclooctene	160	80	50	cyclooctane
	styrene	205	91	85	ethylbenzene

[a] 50 mg. [b] 2.5 ml in 10 ml heptane. [c] ml of H_2 min^{-1} mequiv Ti^{-1}. [d] 0.2 mol.

TABLE 2

SELECTIVITY OF III COMPARED TO I AND II IN THE PHOTOCATALYTIC HYDROGENATION OF SOME LINEAR OLEFINS

Catalyst (precursor)[a]	Olefin[b]	Time (min)	Products (%)
I	isoprene	42	isopentane (40) 2-methylbut-1-ene (54) 2-methylbut-2-ene (5)
	hexa-1,5-diene	9	hex-1-ene (16) *trans*-hex-2-ene (12) hexa-2,4-diene (36) hexane (12)
II	isoprene	32	isopentane (73) 2-methylbut-1-ene (8) 2-methylbut-2-ene (18)
	hexa-1,5-diene	9	hexa-2,4-diene (10) other hexene isomers (42) hexane (41)
III	isoprene	30	2-methylbut-1-ene (60)
	hexa-1,5-diene	30	hex-1-ene (40) hexane (15)

[a] 50 mg. [b] Isoprene: 2.5 ml in 10 ml heptane. Hexadiene: 1.5 ml in 5 ml heptane.

dicate that one of the two alkyl ligands remains in the coordination sphere of the metal during catalysis. It can thus be postulated that photolysis of I and II under hydrogen leads at a primary step to the homolytic cleavage of a Ti—R bond with formation of a metallocarbene species along with the hydrocarbon RH, the R radical abstracting hydrogen from the other alkyl ligand [14]. The carbene subsequently reacts with hydrogen to give an alkyl- or a methylene-bridged hydride dimer of as yet unknown structure which is the reactive catalyst under thermal conditions. Of course a different mechanism should be envisaged for the photoassisted hydrogenation with III.

We monitored the progress of the reaction by ESR at various stages before and after the introduction of the substrate. In all cases a broad signal centered at $g = 1.988$ was obtained in which the Ti hyperfine structure was barely resolved; no appreciable change in intensity was observed in the course of the catalytic reaction, and a rough estimate of the spin density (by comparison with a $(Cp_2TiCl)_2$ standard) showed the presence of paramagnetic species in a ratio of about 5%. No signal attributable to the presence of a titanium(III) hydride was observed.

Conclusion

The alkyltitanocenes described above are discrete molecular precursors which generate catalytically active species in a simple way. They therefore offer the advantage of being amenable to mechanistic studies in a completely homogeneous medium without the complications arising from the introduction of a main-group co-catalyst as is usually the case with the familiar Ziegler systems. Other titanocene compounds such as 1-methylallyltitanocene [17], $Cp_2Ti(CO)(PhC{\equiv}CPh)$ [18], and $Cp_2\overline{Ti\text{-}\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4)Ti}Cp$ [19], are also catalyst precursors showing similar activity under thermal conditions, but their preparation and handling are much more difficult.

Investigations are underway to determine the true nature of the catalysts in the systems described.

Acknowledgements

I am grateful to the Délégation Générale à la Recherche Scientifique et Technique for financial support and to Mrs. J. Hénique for technical assistance.

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