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SILICA-SUPPORTED ANALOGUES OF TITANOCENE

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Summary

Silyl-substituted analogues of bis(cyclopentadienyl)titanium dichloride have been synthesised and attached to silica under mild conditions. Reduction of the complexes thus formed yields active hydrogenation catalysts.

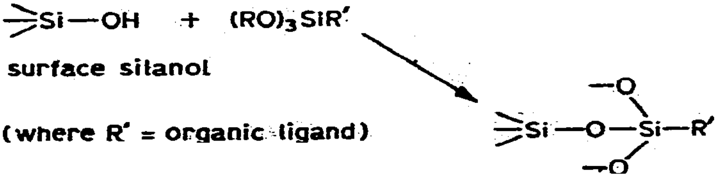
Introduction

The attachment of homogeneous transition metal catalysts to insoluble supports offers the opportunity of extending their usefulness particularly with regard to industrial applications. Consequently, there has been considerable interest in this area recently and although most of the work has been centred on organic polymers [1], inorganic supports can also be used [2]. In general, initial results indicated that these supported catalysts were less active than their homogeneous analogues [3] but, subsequently examples of increased activity [4] and selectivity [5] have appeared. The recently published work by Grubbs [1] on polymer supported titanocene analogues has prompted us to report our results on the related silica supported species.

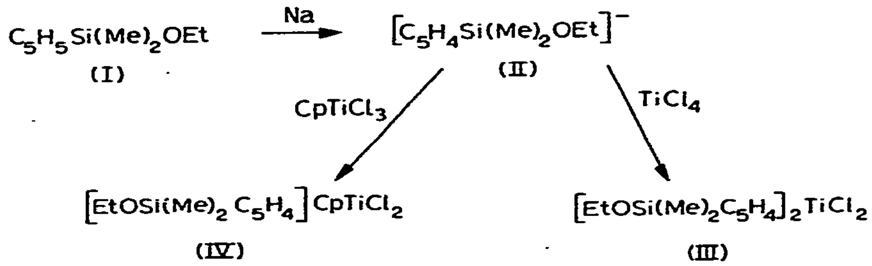
Discussion and results

Titanocene and its hydrides are useful catalysts for the reduction of molecular nitrogen and a variety of olefins. However, the complexes rapidly lose their activity due to dimerisation and polymerisation [6]. We envisaged preventing this dimerisation by attaching the catalyst precursor, Cp_2TiCl_2, to an inorganic support, silica.

The best method of attaching an organic ligand to an inorganic solid such as silica appears to be via the following route [2]:



Therefore, the substituted cyclopentadiene I was synthesised and converted to the titanium complex III by reaction with sodium sand, to generate the anion II, and titanium tetrachloride.



Complex III has previously been synthesised by this route [7] in a high crude yield. We found, however, that this crude product only contains a small percentage of the required bifunctional titanocene dichloride.

Reaction of the anion II with $CpTiCl_3$ gave a low yield of complex IV as a red oil which was identified by its spectroscopic properties (Table 1). Attempts were made to improve the yield of this product in that the anion II was generated by using both isopropyl magnesium bromide and butyllithium. The solvent, temperature and order of addition of the anion and $CpTiCl_3$ were also varied. In every case the major organometallic product was Cp_2TiCl_2 *.

The substituted cyclopentadiene V was also synthesised and reacted sequentially with isopropyl magnesium bromide and titanium tetrachloride to give complex VI as a red solid.

$$\underset{\text{(V)}}{C_5H_5CH_2Si(Me)_2OBu} \xrightarrow[\text{(ii) } TiCl_4]{\text{(i) i-PrMgBr}} \underset{\text{(VI)}}{[BuOSi(Me)_2CH_2C_5H_4]_2TiCl_2}$$

Complex VI is very soluble in most common organic solvents and was only obtained in low yield.

The three titanium complexes III, IV and VI were all stable and reacted with dried silica to give salmon-coloured solids. Reaction occurred readily, even at ambient temperatures, and no complex was removed by Soxhlet extraction with hydrocarbon solvents. Further proof of chemical bonding onto the support was obtained by GLC confirmation of ethanol or butanol formation during the course of the reaction.

Reaction of the supported titanium complexes with butyl lithium or isopropyl magnesium bromide under argon gave grey-green air-sensitive solids which were active catalysts for the reduction of olefins (see Table 2). All the silica-supported titanium catalysts were more active than the homogeneous "titanocene" catalyst for the reduction of terminal olefins but showed similar rates for the reduction of internal olefins. However, whereas the homogeneous catalyst rapidly lost activity, the silica-supported complexes gave a constant

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* In order to confirm that we were generating the anion II efficiently, the reaction with ferrous cloride was undertaken according to the literature [8]. The expected complex, $[EtOSi(Me)_2C_5H_4]_2Fe$, was isolated in high yield. In contrast to the titanium complexes, this ferrocene derivative did not react with silica, even at elevated temperatures, and was recovered unchanged.

TABLE 1

SPECTROSCOPIC DATA FOR SUBSTITUTED TITANOCENE DICHLORIDE COMPLEXES

Complex	^{1}H N.M.R. δ(CDCl$_3$) (ppm)			ν_{max} (KBr) (cm^{-1})		
	Cp	—SiMe$_2$	Other signals	Cp	Si—Me	Si—O—C
[EtOSi(Me)$_2$Cp]CpTiCl$_2$	6.93 and 6.66 (m, 9H)	0.45 (s, 6H)	3.75 (q, 2H) and 1.25 (t, 3H) $\underline{\text{OEt}}$	1435, 1400 1375, 1040 820	1250, 795	1040 (br)
[EtOSi(Me)$_2$Cp]$_2$TiCl$_2$	6.92 and 6.63 (m, 8H)	0.45 (s, 12H)	3.72 (q, 4H) and 1.25 (t, 6H) $\underline{\text{OEt}}$	1445, 1375 1020, 827	1257, 802	1080, 1050
[BuOSi(Me)$_2$Cp]$_2$TiCl$_2$	6.38 and 6.15 (m, 8H)	0.18 (s, 12H)	2.38 (s, 4H $\underline{\text{CH}_2}$—Cp 3.68 (t, 4H), 1.48 (m, 8H) and 1.02 (m, 6H) $\underline{\text{OBu}}$	1485, 1420 1390, 1050 830	1250, 820	1050 (br)

TABLE 2

RATES OF HYDROGENATION OF OLEFINS (10 MMOL IN TOLUENE) USING SILICA SUPPORTED TITANOCENE SPECIES

Catalyst precursor	Rate (ml of H_2/min/mol. equiv. Ti)			
	Ti (mol. equiv.)	1-octene	2-octene	cyclohexene
Non-attached $TiCp_2Cl_2$ [a]	0.01	30 [c]	10 [c]	5 [c]
Silica attached $Ti(EtOSiMe_2Cp)CpCl_2$ [a]	0.02	140	20	7
Silica attached $Ti(EtOSiMe_2Cp)CpCl_2$ [b]	0.02	90	n.d.	n.d.
Silica attached $Ti(EtOSiMe_2Cp)_2Cl_2$ [a]	0.01	150	15	8
Silica attached $Ti(BuOSiMe_2CH_2Cp)_2Cl_2$ [a]	0.01	145	45	8

[a] Activated with BuLi. [b] Activated with C_3H_7MgBr. [c] Uptake of H_2 ceased after ca. 20 min.

rate of reduction over 30 min. This behaviour of the silica-supported species is in contrast to that reported by Grubbs [1] for the polymer-supported catalysts; these showed an increase in rate for both terminal and internal olefins.

The reduction of olefins catalysed by titanocene species requires the presence of an open co-ordination site on the metal [9]. Since such a site is only available on the monomeric species, the increased rate of reduction of terminal olefins with the silica-supported titanocenes suggests an increased concentration of the monomeric species. The reason for the different reactivity of the polymer and silica-supported species is not obvious but may reflect the contrasting physical natures of the supports. Other possible explanations may involve steric factors or even electronic effects due to the substituted cyclopentadienyl ring.

Experimental

All experiments were carried out in a dry atmosphere of argon. The silica was dried by heating under reflux in xylene in a Dean and Stark apparatus. Bis[(dimethylethoxysilyl)cyclopentadienyl]titanium dichloride (III) (7%) was synthesised according to the literature [7].

Bis(dimethylethoxysilyl)ferrocene was synthesised according to the literature [8], $\delta(CDCl_3)$ 4.35 and 4.15 (8H, m, cp), 3.82 (4H, q, OCH_2—Me), 1.22 (6H, t, OCH_2—Me and 0.45 (12H, s, Si—Me).

Cyclopentadienyl[(dimethylethoxysilyl)cyclopentadienyl] titanium dichloride (IV)

To a stirred suspension of sodium sand (1.0 g) in THF was added dropwise dimethylcyclopentadienylethoxysilane (4.2 g) at room temp. After stirring for a further 10 min the reaction mixture was filtered and added to a solution of $TiCpCl_3$ (5.5 g) in THF at —30°C. The mixture was stirred at —20°C for 2 h and then allowed to warm to room temp. overnight. The solvent was removed in vacuo and the residue extracted with chloroform. Removal of the solvent gave a red solid which was extracted with heptane. The red solid residue was identified as $TiCp_2Cl_2$. The heptane-soluble material yielded a red oil (5%) which was identified by spectroscopic methods as complex IV. *m/e* 315 (M^+ — Cl), 286 ($OSiMe_2CpTiClCp$), 221 ($OSiMe_2CpTiCl$).

Changing the solvent to 1,2 dimethoxyethane and using isopropyl magnesium bromide instead of sodium did not increase the yield of complex IV. Varying the reaction temperature and time and order of addition of reactants also did not significantly increase the yield.

Bis[(dimethylbutoxysilylmethyl)cyclopentadienyl] titanium dichloride (VI)

To a solution of $CpCH_2SiMe_2OBu$ [10] (3.5 g; 1.67 × 10^{-2} mol) in 1,2-dimethoxyethane was added dropwise a solution of isopropylmagnesium bromide (1.7 × 10^{-2} mol) in the same solvent. The mixture was stirred overnight at room temp. and added dropwise to a solution of $TiCl_4$ (1.43 g; 0.75 × 10^{-2} mol) in dry benzene. The resulting mixture was stirred at room temp. for 3 h. Removal of the solvent gave a dark brown solid which was extracted with chloroform. The chloroform extract yielded a red solid which was then extracted with hexane to give the crude product which was crystallised at low temp. from hexane to give the complex VI as orange-red crystals, (0.7 g), m.p. 168—172°C. *m/e* 536 (M^+), 501 (M — Cl), 235 ($OSiMe_2CH_2cpTiCl^+$) and 131 ($BuOSiMe_2^+$).

Reaction of the titanium complexes with silica (Grace-Davison 952)

To a stirred suspension of the silica (1 g) in benzene was added a solution of the complex IV (0.4 g) in benzene and the mixture stirred at room temp. for 5 h. The silica was removed by filtration, washed well with acetone and then soxhlet extracted with benzene to yield a salmon-coloured silica (Found: Ti 1.43%). Ethanol was determined in the reaction solution by GLC.

The reaction was repeated in refluxing toluene to give a salmon coloured silica (Found: Ti 2.0%).

Reaction of the complex III with silica in benzene at room temp. gave a pale red coloured silica (Found: Ti 0.7%).

Reaction of the complex VI with silica similarly gave a pale red silica (Found: Ti 0.9%).

Reaction of $TiCp_2Cl_2$ and $[EtOSi(Me)_2Cp]_2Fe$ with silica in refluxing toluene gave colourless silicas which contained no significant amounts of the complexes.

Hydrogenation of the olefins

To a stirred suspension of the silica attached titanium complex (0.01 mol. equiv. Ti) in toluene (5 ml) under argon was added a solution of butyllithium (2 mmol) in hexane (1 ml). The colour of the silica changed from red to grey instantly. The apparatus was then evacuated and filled with hydrogen at 1 atmos. The olefin (10 mmol) was added and the rate of hydrogen uptake measured. The final solution was analysed by GLC. Only the expected hydrogenation products were detected.

An active hydrogenation catalyst was also produced by activation with isopropyl magnesium bromide.

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