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SILICA-SUPPORTED CYCLOPENTADIENYL-RHODIUM(I), -COBALT(I), AND -TITANIUM(IV) COMPLEXES

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Summary

The silylated cyclopentadiene derivative, $(MeO)_3Si(CH_2)_3C_5H_5$, synthesised from commercially-available $(MeO)_3Si(CH_2)_3Cl$, has been used to prepare the complexes $[\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4]Rh(CO)_2$, $[\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4]Rh(COD)$ (COD = cyclo-octa-1,5-diene), and $[\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4]_2TiCl_2$. The complex $[\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4]TiCl_3$, prepared by reaction of $NaC_5H_4(CH_2)_3Si(OMe)_3$ with $TiCl_4$ (1/1 molar ratio) and also by reaction of $[\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4]Ti(OEt)_3$ with CH_3COCl, proved to be very unstable. Attempts to synthesise the complex $[\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4](\eta^5\text{-}C_5H_5)TiCl_2$, either by reaction of $[\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4]TiCl_3$ with NaC_5H_4 or reaction of $(\eta^5\text{-}C_5H_5)TiCl_3$ with $NaC_5H_4(CH_2)_3Si(OMe)_3$, gave none of the expected product and only $(\eta^5\text{-}C_5H_5)_2TiCl_2$ could be isolated from these reactions. The cyclo-octadiene rhodium complex supported on silica has been shown to be an efficient cyclotrimerization catalyst, and the silica-supported titanium complex $SIL\text{-}(CH_2)_3C_5H_4)_2TiCl_2$ is, after reduction with butyllithium, an efficient and selective catalyst for the hydrogenation of alk-1-enes.

Introduction

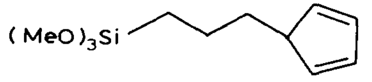
The "heterogenisation" of homogenous transition metal catalysts by attachment to organic polymers [1] and inorganic supports [2] has received a great deal of attention in recent years since such catalysts often combine the most advantageous properties of both the homogeneous and heterogeneous systems. In the main, attention has been focussed on supported phosphine and amine ligands, but there is growing interest in the development of catalysts based on supported cyclopentadienyl ligands. So, for example, transition metal catalysts have been synthesized having titanium [3–5], zirconium [5], hafnium [5], rhodium [6,7], cobalt [6–9], and iron [10] attached to cross-linked polystyrene by a cyclopentadiene ligand. Some of these complexes have been shown to be active catalysts for hydrogenation [3–6,8], cyclotrimerization of acetylenes [6], and the Fischer–Tropsch synthesis [9], Recently, Stille [11] has described cobalt and rhodium cyclopentadienyl complexes which are supported on poly(phenylene oxide).

There are some difficulties inherent in the use of commercially-available cross-linked polystyrene beads as a support. It is difficult to control in a meaningful way the loading of the functional ligand on to the polymer as the degree of cross-linking in the polymer and the extent of swelling of the polymer lattice in the solvent used can both affect accessibility of reactants to the catalyst sites. In contrast, the rigid matrix of an inorganic support, such as silica, can offer some advantages over the organic supports in certain cases. Loadings on silica tend to be much lower than on organic support, typically 0.1 mmol g^{-1} [12], and catalysts which can become deactivated by dimerisation or cluster formation should have longer lifetimes on these supports. Most of the work carried out on silica-supported catalysts has concentrated on phosphine-metal complexes [2] following the pioneering work of Pitkethly et al. [13]. However, Thompson et al. [14] have reported the titanium(IV) complex, $[(EtO)Me_2SiC_5H_4]_2TiCl_2$ prepared in 7% yield from $(EtO)Me_2SiC_5H_5$, and Brintzinger [15] has described cobalt and iron complexes based on $(EtO)_3SiC_5H_5$.

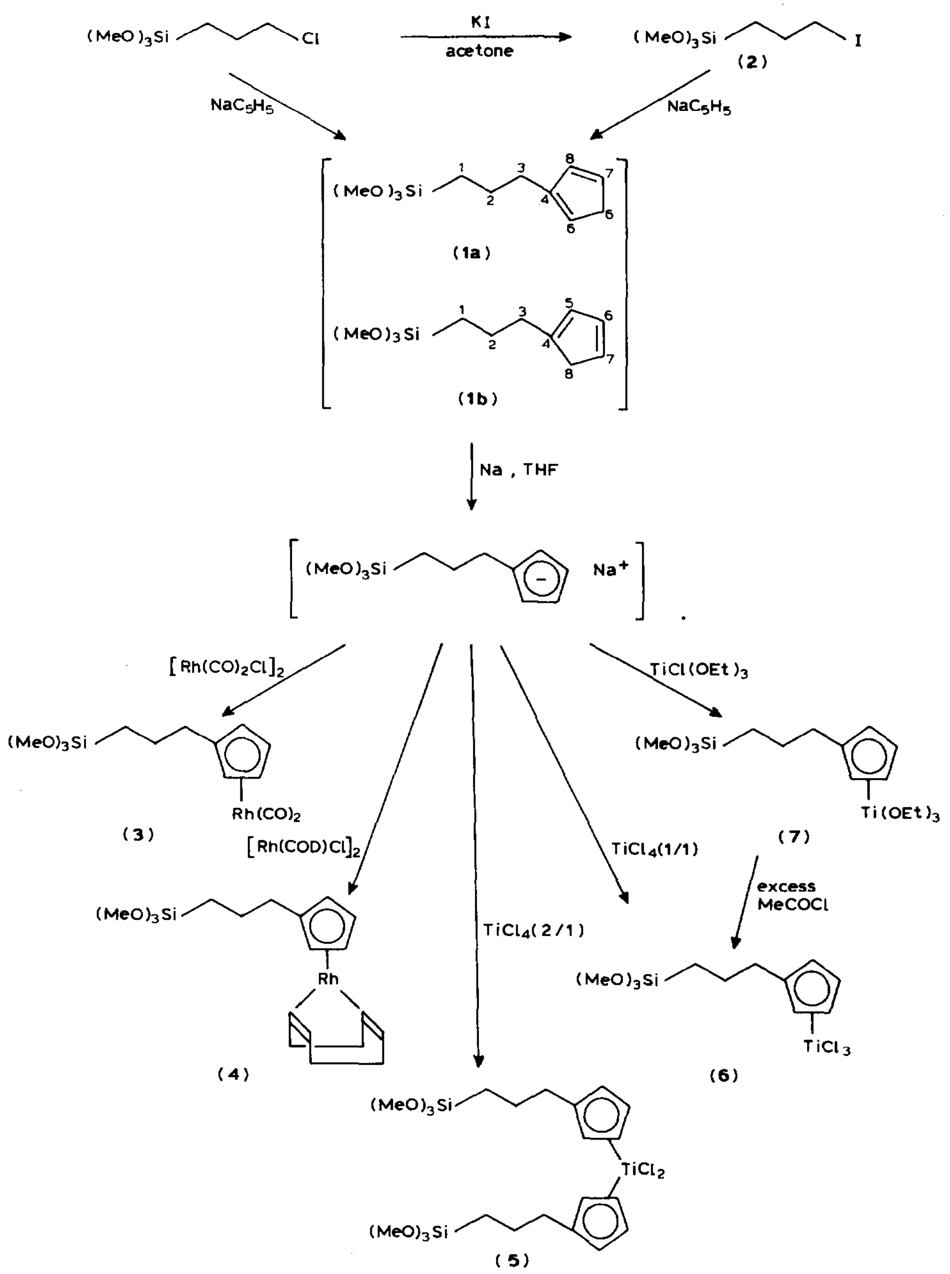
We now report a simple synthetic sequence starting from the commercially available compound, $(MeO)_3SiCH_2CH_2CH_2Cl$, to provide the cyclopentadiene derivative, $(MeO)_3Si(CH_2)_3C_5H_5$, which has been used routinely for the preparation of rhodium(I) and titanium(IV) complexes. Some catalytic applications of these supported complexes are described.

Results and discussion

Reaction between sodium cyclopentadienide and $(MeO)_3SiCH_2CH_2CH_2Cl$ is slow in tetrahydrofuran at room temperature, and even after 72 h GLC analysis of the reaction mixture indicated only a 38% conversion to the required product (**1**). Pinnavaia et al. [16] have reported that **1** can be obtained from the chloro derivative and NaC_5H_5 in tetrahydrofuran at 50°C over 4 h. In our hands reaction at the reflux temperature of tetrahydrofuran gave a 50% conversion after 20 h, but continued reflux resulted in no further increase in the amount of **1**, and dicyclopentadiene started to appear in the product mixture. A much improved yield of **1** was obtained by first converting the chloro derivative to the iodo compound **2** by heating under reflux with a slight excess of sodium iodide in dry acetone for 24 h. GLC analysis indicated a quantitative yield, and after distillation **2** is obtained in 85% yield as a colourless oil. Purification by distillation is essential to remove all traces of acetone as this can react with NaC_5H_5 in the next stage to give bright yellow dimethylfulvene which is difficult to remove. Compound **2** reacts vigorously over a few minutes on addition of sodium cyclopentadienide in tetrahydrofuran at room temperature to give **1** in 80% isolated yield as a golden yellow oil. From the



(1c)



SCHEME 1

complexity of the ^1H and ^{13}C NMR spectra it is apparent that **1** is an approximate 1/1 mixture of the two isomers (**1a** and **1b**, see Scheme 1), but the third possible isomer **1c** is not formed.Regular examination of the ^{13}C NMR spectrum of a neat sample of **1** kept at room temperature showed no evidence of dimerisation over a period of 2 weeks.

The reaction of **1** with sodium sand is slow at room temperature in tetrahydrofuran, and formation of the cyclopentadienide ion was not complete even after 18 h using 1 mol equivalent of sodium. Addition of the solution to a solution of $[Rh(CO)_2Cl]_2$ in diethyl ether at room temperature gave only a moderate yield (45%) of the desired product **3** as a red oil, characterised by ^1H NMR spectroscopy and the presence of two characteristic [18] strong, sharp metal carbonyl stretching vibrations in the IR spectrum. Better results were obtained using an excess of sodium to form the cyclopentadienide ion, but 20% of the starting mateial remained even after 18 h. Reaction of the cyclopentadienide ion with $[RhCl(COD)]_2$ in tetrahydrofuran was slow, and TLC monitoring indicated that a reaction time of at least 18 h is required. The product **4** was isolated in 58% yield after chromatography as a yellow oil. The ^{13}C NMR spectrum shows a 2 Hz coupling between the C atoms of the cyclopentadienyl ligand and rhodium, and a 16 Hz coupling between the rhodium atom and the alkenyl C atoms of the cyclooctadiene ligand, in reasonable agreement with the values reported (J(Rh–Cp) 0 Hz; J(Rh–COD) 14 Hz) for $[(\eta\text{-}C_5H_5)Rh(COD)]$ [19]. The compound was not sufficiently volatile to give a conventional mass spectrum, but an excellent spectrum was obtained using the FAB technique and this has been reported elsewhere [20]. In 1,2-dimethoxyethane the reaction between $(MeO)_3Si(CH_2)_3C_5H_4Na$ (2 mol) and cold $TiCl_4$ (1 mol) gave only a 20% yield of complex **5** which was isolated as a moisture- and air-sensitive red oil. An improved yield (55%) of **5** was obtained by carrying out the reaction in tetrahydrofuran. Complex **5** has been fully characterised by IR, ^1H, and ^{13}C NMR spectroscopy, and mass spectrometry. Attempts to prepare $[\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4]TiCl_3$ (**6**) by reaction of $(MeO)_3Si(CH_2)_3C_5H_4Na$ (1 mol) with $TiCl_4$ (1 mol) in tetrahydrofuran was less successful. The product was obtained in ca. 21% yield as a thick red oil, distinguishable from compound **5** by the presence of an intense IR band at 770 cm^{-1}, which is absent from the spectrum of **5**. A similar band has been noted previously by Gorsich [21] and Sloan and Barber [22] when comparing the IR spectra of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and $(\eta^5\text{-}C_5H_5)TiCl_3$. The trichlorotitanium(IV) complex decomposes rapidly, and even when stored under dry nitrogen at −10°C it gradually turned brown and later green over a period of 6 h. An alternative route to **6** was explored involving the initial reaction between $(MeO)_3Si(CH_2)_3C_5H_4Na$ and $Ti(OEt)_3Cl$ in tetrahydrofuran to give a 73% yield of $(MeO)_3Si(CH_2)_3C_5H_4Ti(OEt)_3$ (**7**) as a yellow oil. Reaction of **7** with an excess of acetyl chloride at 0°C, followed by removal of the ethyl acetate formed, gave **6** in 85% yield, but all attempts to store the material for longer than a few hours proved unsuccessful.

Attempts have also been made to synthesise the mixed cyclopentadienyl titanium(IV) complex, $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4]TiCl_2$ (**8**). When crude complex **6**, prepared from $[\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4]Ti(OEt)_3$, was caused to react with an excess of NaC_5H_5 in tetrahydrofuran at room temperature, the only titanium-containing product isolated from this reaction was $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$ in 56% yield. In a further attempt to prepare **8** pure $(\eta^5\text{-}C_5H_5)TiCl_3$ was caused to react with an excess of $(MeO)_3Si(CH_2)_3C_5H_4Na$ in tetrahydrofuran at −30°C, but, again, the only titanium complex isolated was $(\eta^5\text{-}C_5H_5)_2TiCl_2$ in 41% yield. A similar observation has been made previously by Jackson et al. [14], who found that $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$ was the major product formed upon reaction between $\eta^5\text{-}C_5H_5TiCl_3$ and an excess of $(EtO)Me_2SiC_5H_4Na$ in tetrahydrofuran at −30°C.

TABLE 1

CYCLOMERIZATION OF ALKYNES USING RECYCLED SILICA-SUPPORTED RHODIUM CATALYST

Run	[alkyne] (mol)	k (10^{-3} mol min^{-1})	Initial rate (10^{-3} min^{-1})
DMAD			
1	0.76	1.88 ± 0.13	1.50
2	0.33	0.40 ± 0.03	0.33
3	0.70	0.20 ± 0.06	0.17
4 [a]	035	1.46 ± 0.42	0.95
Hex-3-yne			
5	0.70	0.27 ± 0.03	0.26

[a] After prolonged extraction of the catalyst with dichloromethane.

The expected product $[\eta^5\text{-(EtO)Me}_2\text{SiC}_5\text{H}_4](\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2$ could be isolated in only 5% yield after several attempts, despite the fact that the anion $\text{(EtO)Me}_2\text{SiC}_5\text{H}_4\text{Na}$ was found to be produced in high yield.

Immobilisation on silica

The rhodium complex **4** was immobilised on silica at 80°C for 4 h in toluene solution to give a pale orange solid [loading 0.51 mmol (g silica)$^{-1}$], which turned bright green on exposure to air. This supported complex was found to be an active catalyst for the cyclotrimerisation of dimethyl acetylenedicarboxylate (DMAD) to hexacarbomethoxybenzene (82% yield) in refluxing toluene. During the reaction the colour of the catalyst changed from pale orange to brick red and became air-stable indicating that the nature of the complex had changed during the catalysis cycle; the new complex was also an active cyclotrimerization catalyst (vide infra). A kinetic study of the cyclomerization reaction established that it was first order in acetylene concentration, as found previously [23] for the similar reaction catalyzed by $(\eta^5\text{-C}_5\text{H}_5)\text{Rh(COD)}$. The catalytic activity of the supported catalyst [2.2×10^{-3} mol min^{-1} (g. atom Rh)$^{-1}$] was only slightly poorer than that of the homogeneous analogue $(\eta^5\text{-C}_5\text{H}_5)\text{Rh(COD)}$ [3.72×10^{-3} mol min^{-1} (g. atom Rh)$^{-1}$], but the activity of the supported catalyst in the cyclotrimerisation of DMAD declined markedly on recycling (Table 1).

This decline in activity was not due to loss of rhodium from the silica, but appears to be due mainly to build up of a polymer on the surface of the catalyst. DMAD is known to polymerise on prolonged heating [23], and after prolonged Soxhlet extraction by dichloromethane the activity of the catalyst returned to a much higher level. Some support for this assumption is that microanalysis of the catalysts shows an increase in the C and H content from C (7.7%) and H (1.7%) after one cyclotrimerization reaction to C (10.6%) and H (1.8%) after three cyclotrimerization reactions. The brick red supported catalyst, isolated after use for the cyclotrimerization of DMAD, was also found to be an effective catalyst for the cyclotrimerization of hex-3-yne (see Table 1) although the rate of reaction is much slower, as found also with the homogeneous complex $(\eta^5\text{-C}_5\text{H}_5)\text{Rh(COD)}$ [23].

For immobilization of the titanium complex **5** on silica (Grace-Davison 952) it was necessary to carry out the reaction in toluene at room temperature. At higher

TABLE 2

RATE OF HYDROGENATION (cm^3 H_2 min^{-1} mmol Ti^{-1} atm^{-1}) WITH [SIL-$(CH_2)_3C_5H_4]_2TiCl_2$ (2.8% Ti; 0.012 mmol) AND AN EXCESS OF BUTYLLITHIUM

Olefin	Rate	Conversion after 3 h
1-octene	716	100
1-octene (recycle)	485	100
2-octene (*trans*)	1.74	9 (after 48 h)
cyclohexene	0.61	10 (after 48 h)
4-methyl-1-pentene	711	100
2-methyl-1-pentene	9.2	11
4-vinylcyclohex-1-ene	134.8	24 [a]
1-heptene	760.3	100
cyclo-octene	36.9	21
α-methylstyrene	0.0	0
styrene	0.0	0
cycloheptene	13.9	13 (after 36 h)

[a] Ethylcyclohex-1-ene product.

temperature exchange of the surface hydroxyl groups with the Ti-Cl ligands competes with the desired exchange with the $(MeO)_3Si$-terminus leading to catalyst deactivation. Upon reduction with butyllithium in an atmosphere of hydrogen at room temperature the silica-supported titanium complex proved to be an efficient and selective hydrogenation catalyst (see Table 2). For comparison, the rates of hydrogenation with the homogeneous catalysts $(\eta^5\text{-}C_5H_5)_2TiCl_2$, $(\eta^5\text{-}MeC_5H_4)\text{-}TiCl_2$, $[(MeO)_3Si(CH_2)_3C_5H_4]_2TiCl_2$, $(\eta^5\text{-}C_5H_5)TiCl_3$ and $(\eta^5\text{-}MeC_5H_4)TiCl_3$ were determined under similar conditions and are reported in Table 3. The relative activities of the homogeneous catalysts were found to be in the order $(\eta^5\text{-}MeC_5H_4)$-

TABLE 3

RATES OF HYDROGENATION (cm^3 H_2 min^{-1} mmol Ti^{-1} atm^{-1}) WITH HOMOGENOUS TITANIUM CATALYSTS

Olefin	Catalyst					
	$C_{p2}TiCl_2$/BuLi [a]		$(MeC_5H_4)_2TiCl_2$/BuLi		$[(MeO)_3Si(CH_2)_3C_5H_4]_2$-$TiCl_2$/BuLi	
	Rate	Conv. (%) 4 h	Rate	Conv. (%) 4 h	Rate	Conv. (%) 4 h
1-heptene	17.2	100	72.05	100		
4-methyl-1-pentene	12.3	100	27.68	100		
1-octene	11.7	100	17.5	100	30.2	68
1-octene (*trans*)	8.4	66	48.6	62	14.1	41
2-methyl-1-pentene	6.0	51	19.6	63		
cyclo-octene	5.6	72	31.7	58		
cyclohexene	4.0	45	15.9	53	8.21	20
cycloheptene	4.8	60	19.1	51		
α-methylstyrene	0.6	12	8.79	16		
styrene	3.6	32	21.7	26		
4-vinylcyclohexene	4.0	62	22.7	51		

[a] 0.32 mmol Ti.

$TiCl_2 > [\eta^5\text{-}(MeO)_3Si(CH_2)_3C_5H_4]_2 > (\eta^5\text{-}C_5H_5)TiCl_3 > (\eta^5\text{-}C_5H_5)_2TiCl_2 > (\eta^5\text{-}MeC_5H_4)TiCl_3$ and the rate decreases as alk-1-ene > alk-2-ene > cycloalkene suggesting that the reaction is mainly controlled by steric factors, although electronic factors do have some influence as evidenced by the effect of substituents in the cyclopentadienyl ring. Interestingly, the effect of substitution in the $(\eta^5\text{-}C_5H_5)TiCl_3$ series appears to be the reverse of that found for the $(\eta^5\text{-}C_5H_5)_2TiCl_2$ series.

It can be seen by comparison of the results presented in Tables 2 and 3 that the silica-supported catalyst is not only a more active catalyst than any of the homogenous analogues, but it is far more selective towards alk-1-enes. The hydrogenation of 4-vinylcyclohex-1-ene using the supported catalyst is slow and requires 60 h for complete conversion. GLC and spectroscopic analysis showed only a single product, 1-ethylcyclohexene, implying selective hydrogenation of the exocyclic double bond an isomerisation of the ring double bond to the thermodynamically most stable alkene. A similar isomerisation of 1,3-cyclooctadiene to 1,5-cyclooctadiene has been reported by Grubbs for a titanocene derivative attached to a 20% styrene-divinylbenzene copolymer [24]. The organic-supported catalyst (reported rates of hydrogenation 213, 90 and 1 cm^3 H_2 min^{-1} mmol Ti^{-1} atm $^{-1}$ for 1-hexene, cyclohexene

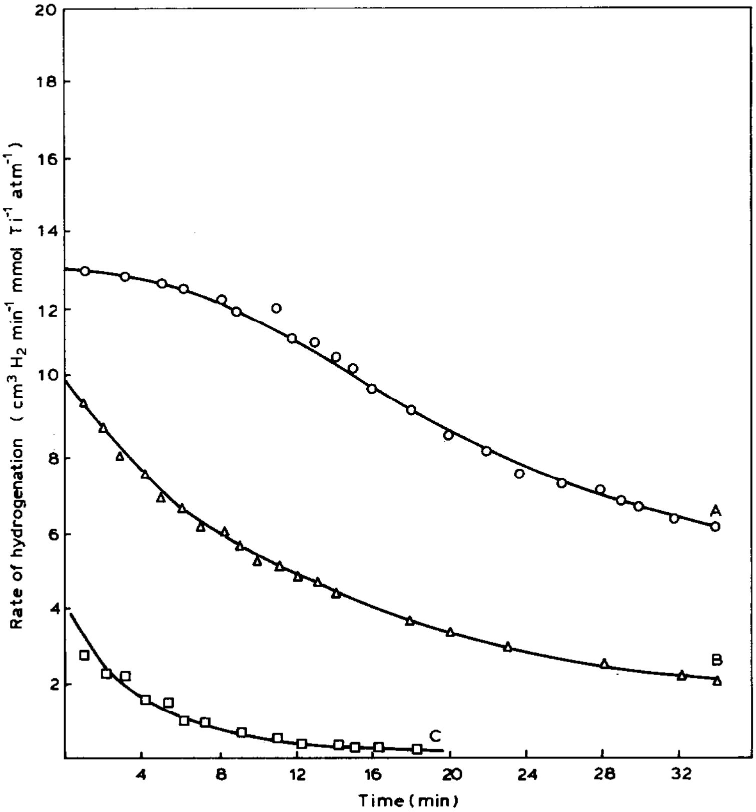


Fig. 1. Rate-time curves for hydrogenation of oct-1-ene A. $[\textcircled{\scriptsize Si}(CH_2)_3C_5H_4]_2TiCl_2/BuLi$; B. $[(MeO)_3Si(CH_2)_3C_5H_4]_2TiCl_2/BuLi$; C. $(C_5H_5)_2TiCl_2/BuLi$.

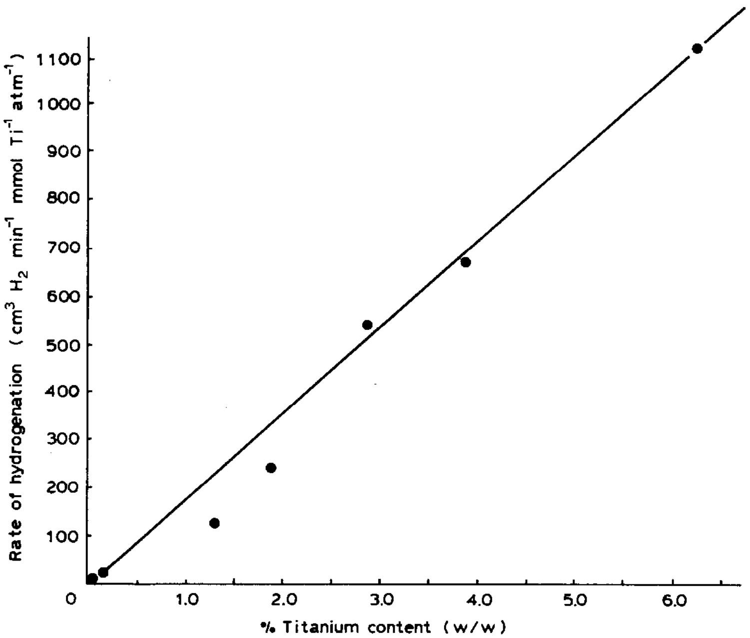
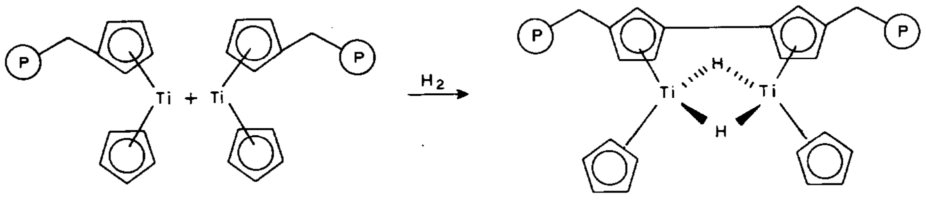


Fig. 2. Effect of titanium loading on the rate of hydrogenation of 1-octene using $[SIL\text{-}(CH_2)_3C_5H_4]_2TiCl_2$ catalyst.

and methylcyclohexene respectively [4]) appears to be less active than the silica-supported catalyst. More importantly, the polymer-supported catalyst became totally inactive after approximately 2 h, presumably by dimerisation to the inactive species **9** by a similar mechanism to that known to occur rapidly with titanocene under hydrogenation conditions [25]. In contrast the silica-supported catalyst still showed high activity after 2 days.



(9)

This difference in the rates of decay of the homogeneous catalysts and the silica-supported catalyst is also clear from the rate profiles for hydrogenation with the homogeneous and supported catalyst. The silica-supported catalyst does decay but only slowly (see Fig. 1). A marked difference between the polymer- and silica-supported catalysts is also seen on examination of the effect of the titanium loading on the rate of hydrogenation of oct-1-ene (see Fig. 2). At higher loadings there is a linear relationship between the rate of hydrogenation and the titanium loading. This relationship does not hold for low loadings where appreciable exchange of the surface silanol groups with the Ti–Cl bonds occurs reducing the activity per titanium atom [26]. At the higher loadings [0.59 to 1.25 mmol Ti (g silica)$^{-1}$ it is calculated that there is one titanium atom occupying an area of between 0.37 to 0.79 nm^2 of the silica surface. This suggests a close packing of the hydrocarbon chains in such a way that two titanocene moieties cannot easily interact. This contrasts with the organic polymer supported catalyst where hydrogenation of hex-1-ene increases approximately linearly with titanium loading up to a maximum loading of 0.14 mmol Ti (g polymer)$^{-1}$ and thereafter the rate of hydrogenation decreases with increased titatium loading due to deactivation by dimerisation to a complex of type **9** [27].

Experimental

(3-Chloropropyl)trimethoxysilane was a commercial sample (Fluorochem Ltd) used without purification. Bis(η^5-cyclopentadienyl)dichlorotitanium(IV) [28], bis(η^5-methylcyclopentadienyl)dichlorotitanium(IV) [29], (η^5-cyclopentadienyl)trichlorotitanium(IV) [21,30], and (η^5-methylcyclopentadienyl)trichlorotitanium(IV) [31] were prepared by previously reported procedures. Sodium iodide was dried at 300°C for 4 h. All solvents were purified and dried by standard procedures, and except where stated all reactions were carried out under nitrogen purified by passage through a column packed with copper on charcoal maintained at 300°C.

IR spectra were recorded on a Perkin–Elmer Infracord 735 spectrophotometer and far IR spectra were determined using a Beckman IR 720M spectrophotometer. ^{1}H NMR spectra were recorded on a Perkin–Elmer R32 (90 MHz) or R34 (220 MHz) instrument, ^{13}C NMR spectra on a Bruker WP80 (20.1 MHz) instrument, and mass spectra on Kratos 2 spectrometer, except for fast atom bombardment spectra which were determined on solutions in tetraethylene glycol and tetraglyme (1/1 v/v) using an AEI MS 902 instrument.

Preparation of (3-iodopropyl)trimethoxysilane

(3-Chloropropyl)trimethoxysilane (11.92 g, 60 mmol) was added to a solution of anhydrous sodium iodide (9.0 g, 60 mmol) in dry acetone (100 cm^3), and the mixture was heated under reflux for 24 h when GLC analysis (4 m PEGA on Celite column at 190°C) showed $>95\%$ complete reaction. The solvent was removed under reduced pressure, and addition of dry diethyl ether to the residue followed by filtration of the sodium chloride, and removal of the ether gave compound **2** as a pale yellow liquid (11.0 g, 51 mmol, 85%) b.p. 80°C/8 mmHg. (Found: C, 25.0; H, 5.4; I, 43.7. $C_6H_{15}IO_3Si$ calcd.: C, 24.82; H, 5.1; I, 43.7%). IR (neat liquid): ν 2930s (C–H str., CH_3), 2825s (C–H str, CH_2), 1450m (C–H def, CH_3), 1440m, 1410m, 1320m (C–H def.), 1290m, 1270m, 1210m (C–O str.). 1190m, 1100br.s (C–O str), 990m, 959m, 920m, 898s, 810s, 760m (C–H def.) cm^{-1}. ^{1}H NMR (neat, 90 MHz, Me_4Si ext. ref.) δ 0.9 (t, 2H, J 7 Hz, CH_2Si), 2.0 (sextet, 2H, J 7 Hz, CH_2), 3.4 (t, 2H, J 7 Hz, I-CH_2), 3.7 (s, 9H, CH_3O) ppm. MS m/z, No M^+, 187 [$M^+ - 3(OMe)$] 5.6%, 163 [$(CH_2)_3SiOMe$]$^+$ 11.1%, 121 [$Si(OMe)_3$]$^+$ 100%, 59 [$SiOMe$]$^+$ 12.1 %.

Preparation of (3-cyclopentadienylpropyl)trimethoxysilane

(a) From (3-chloropropyl)trimethoxysilane. (3-Chloropropyl)trimethoxysilane (11.92 g, 60 mmol) was added by means of a syringe to a solution of sodium cyclopentadienide [from cyclopentadiene (3.96 g, 5.0 cm^3, 60 mmol) and sodium

sand (1.38 g, 0.06 g atoms)] in tetrahydrofuran (25 cm^3), and the mixture was stirred at room temperature for 72 h. Removal of the solvent under reduced pressure and addition of light petroleum (b.p. 30–40°C) gave a brown precipitate which was removed by filtration. Removal of the solvent from the filtrate gave a clean yellow oil (8.84 g) shown by GLC (4 m PEGA column at 190°C) to contain (3-cyclopentadienylpropyl)trimethoxysilane (5.13 g, 22.5 mmol, 38%) and starting material. Attempts to separate these by distillation under reduced pressure resulted in appreciable coking.

(b) From (3-iodopropyl)trimethoxysilane. A solution of sodium cyclopentadienide was prepared by reacting freshly-prepared cyclopentadiene monomer (6.0 g, 0.9 mmol) and sodium sand (2.07 g, 0.09 g atom) in dry tetrahydrofuran (250 cm^3) at room temperature. The resulting faint pink solution was then added dropwise to a solution of 3-iodopropyltrimethoxysilane (25.0 g, 0.086 mmol) in dry tetrahydrofuran (60 cm^3). After the addition, the reaction mixture was stirred for 3 h and the solvent was evaporated in vacuo. The residue was extracted repeatedly (3 × 70 cm^3) with dry petroleum ether b.p. 40–60°C and filtered. The filtrate was evaporated in vacuo and the crude product was distilled under reduced pressure to give two fractions. The first, b.p. 30°C/0.5 mmHg, was identified by IR spectroscopy as unchanged 3-iodopropyltrimethoxysilane (5.2 g, 0.018 mmol). The second, a golden yellow oil b.p. 58°C/0.5 mmHg, was the desired product, (3-cyclopentadienylpropyltrimethoxysilane (16.0 g, 0.069 mmol, 80%), shown to be 95% pure by GLC (Found: C, 58.4; H, 9.3. $C_{11}H_{20}O_3Si$ calcd.: C, 57.9; H, 8.9%).

The ^1H and ^{13}C NMR spectra of this product indicated that it was a mixture of the two isomers **1a** and **1b** in an approximate 1/1 ratio. IR (neat liquid): ν 3050m (C–H str.), 2950s, 2830s, (C–H str.), 1600–1590 br.m (C–C str.), 1450m (C–H def.), 1400m, 1360m, 1330m (C–H def.), 1180–1100 br.s (C–O str.), 990m, 890s, 810s, 670m (C–H def.) cm^{-1}. ^1H NMR (neat liquid, 90 MHz, Me_4Si ext.ref.) δ 0.3 (t, 2H, J 7 Hz, CH_2-Si), 1.4 (sextet, 2H, J 7 Hz, CH_2), 2.1 (m, 2H, CH_2 ring), 2.5 (m, 2H, $CH_2CH=$, J 8 Hz), 3.15 (s, 9H, CH_3O), 6.05 (m, 1H, CH=), 5.7 (m, 1H, CH=), 5.65 (m, 1H, =CH) ppm. ^{13}C NMR ($CDCl_3$) 8.56 (Si-CH_3), 21.65 ($\mathit{C}H_2$-CH_2Si), 32.29 ($\mathit{C}H_2$-Cp), 33.29 (CH_2-Cp), 40.46 (CH_2 of Cp ring) 42.36 (CH_2 of Cp ring), 49.24 ($\mathit{C}H_3O$), 125.5, 126.2, 129.7, 131.9, 134.2, 146.4, 148.7 (-C=) ppm; MS m/z 228 $[M]^+$ 8.2%, 196 $[M - MeOH]^+$ 21.3, 168$[M - MeOH - C_2H_4]^+$ 10.5%, 121 $[(MeO)_3Si]^+$ 100%, 106$[CH_2{=}CHCH_2C_5H_5]^+$ 5.8%, 91$[(MeO)_2SiH]^+$ 34.4%, 80$(C_6H_8)^+$ 21.8%, 77$(C_6H_5)^+$ 5.7%.

Preparation of [η^5-(trimethoxysilylpropyl)cyclopentadienyl]dicarbonylrhodium

The deep orange solution of sodium (trimethoxysilylpropyl)cyclopentadienide (10 mmol), prepared by stirring (3-cyclopentadienylpropyl)trimethoxysilane (2.19 g, 10.0 mmol) with sodium sand (0.23 g) at room temperature for 10 h, was added in one portion by means of a syringe to a solution of $[Rh(CO)_2Cl]_2$ (1.94 g, 5.0 mmol) in diethyl ether (5 cm^3). On stirring at room temperature for 18 h the solution gradually turned brown, and removal of the solvent gave a brown gum. This was extracted with light petroleum (b.p. 30–40°C, 3 × 5 cm^3), and the extract chromatographed (Florisil, diethyl ether eluant) to give the compound **3** as a clear red oil (1.69 g, 4.5 mmol, 45%). IR (neat) ν(CO) 1985s, 2020 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.8 (t, 2H), 1.6 (m, 2H), 2.3 (m, 2H), 3.53 (s, 9H), 4.95 (d, 2H, J 2 Hz) 5.12 (d, 2H, J 2 Hz) ppm.

Preparation of [η^5-(trimethoxysilylpropyl)cyclopentadienyl](cyclo-octa-1,5-diene)rhodium

Addition of a solution of sodium(trimethoxysilylpropyl)cyclopentadienide (10 mmol) in tetrahydrofuran (5 cm^3) to a solution of [(COD)RhCl]$_2$ (2.46 g, 5 mmol) in the same solvent followed by stirring at room temperature for 18 h gave a brown solution. TLC analysis (silica, 50/50, CH_2Cl_2/light petroleum) showed that the rhodium starting material had disappeared. After removal of the solvent the residue was extracted with diethyl ether (3 × 5 cm^3), and the extract chromatographed to give compound **4** as a clear yellow oil (2.48 g, 5.8 mmol, 58%). [^{1}H NMR ($CDCl_3$) δ 0.8 (m, 2H), 1.5–2.4 (m, 12H), 3.53 (s, 9H), 3.75 (s, 4H), 4.95 (d, 2H, *J*(Rh–H) 2 Hz), 5.12 (d, 2H, J(Rh–H) 2 Hz) ppm. ^{13}C NMR (off resonance decoupled) 8.85 (t), 23.85 (t), 30.65 (t), 32.19 (s), 50.04 (q), 62.99 (d), *J*(Rh–C) 2 Hz), 84.58 (d, *J*(Rh–C) 16 Hz), (d, *J*(Rh–C) 16 Hz) 106.02 (s).

Preparation of bis[η^5-(trimethoxysilylpropyl)cyclopentadienyl]dichlorotitanium(IV)

A solution of sodium (trimethoxysilylpropyl)cyclopentadienide (48 mmol) in tetrahydrofuran (250 cm^3) was added to a solution of titanium tetrachloride (4.57 g, 24 mmol, 2.64 cm^3) in the same solvent at −65°C. The mixture was stirred at −30°C for 2 h and then allowed to warm up to room temperature and stirred for a further 16 h. Removal of the solvent and extraction of the residue with anhydrous chloroform (3 × 100 cm^3), and removal of the solvent from the extract gave a red oil, which was then extracted with heptane, the extract filtered, and solvent removed to give complex **5** (7.6 g, 35 mmol, 55%).

(Found: C, 45.2; H, 5.9; Cl, 8.2. $C_{22}H_{38}Cl_2O_3Ti$ calcd.: C, 45.9; H, 6.95; Cl, 12.34%). IR (neat liquid): ν 3110m (C–H str), 2960s, 2850s, 2930s (C–H str.), 1490m (C–H def.), 1461m, 1415m, (C–H def.), 1190–1100 br.s (C–O str.), 870m, 810s (C–H def.), 710–660br (C–H def.) cm^{-1}. Far IR ν 468 asym Ti-Cl, 460 asym (Ti–Cl), 434 sym (Ti–Cl), 348 sym (Ti–vinyl) 306 (tilt) 266 (tilt), 190 def. sym (Cp–Ti–Cp), 100 def. sym. (Cl–Ti–Cl) cm^{-1}. ^{1}H NMR ($CDCl_3$, 220 MHz, Me_4Si ext. ref.) δ 0.65 (t, 2H, *J* 7 Hz, CH_2–Si), 1.65 (sextet, 2H, CH_2), 2.7 (t, 2H, *J* 7 Hz, CH_2–C_5H_4), 3.55 (s, 9H, CH_3O), 6.35 and 6.45 (d, 4H, C_5H_4) ppm. ^{13}C NMR ($CDCl_3$) 0.90 (CH_2–Si), 29.6 (CH_2), 34.1 ($CH_2C_5H_4$), 50.5 (CH_3O), 115.8 (*C*H=) 122.3 (–CH=), 139.5 [–C– $(CH_2)_3$]ppm. MS[FAB] in TEG (1/1 v/v) *m/z* 537 $[M-Cl]^+$, 502 $[M-CL]^+$, 445 $\{[(MeO)_3Si(CH_2)_3C_5H_4]_2H\}^+$, 345 $[M-(MeO)_3Si(CH_2)C_5H_4]^+$, 310 $[(MeO)_3Si(CH_2)C_5H_4TiCl]^+$, 121 $[(MeO)_3Si]^+$.

Preparation of [η^5-(trimethoxysilylpropyl)cyclopentadienyl]triethoxytitanium(IV)

A solution of sodium (trimethoxysilylpropyl)cyclopentadienide (37.0 mmol) in tetrahydrofuran (300 cm^3) was added dropwise to a cold (0°C) solution of triethoxychlorotitanium (8.12 g, 37.0 mmol) in the same solvent (30 cm^3), and the mixture was stirred at 0°C for 1 h and for a further 3.5 h while warming up to room temperature. The NaCl which formed was removed by filtration and the solvent was removed from the filtrate to give a red oil, which was purified by distillation to give **7** as a yellow oil (11.07 g, 27.0 mmol, 73%) b.p. 140°C/0.7 mmHg GLC analysis showed > 95% purity. (Found: C, 50.7; H, 8.7. $C_{17}H_{34}O_6$ SiTi calcd.: C, 49.8; H, 8.3%). IR (neat liquid): ν 3050m (C–H str), 2950s, 2900s, 2800s, 2790s, (C–H str.), 1500w, (C–C str.), 1450m, 1380m, 1360m, 1280m, (C–H def.), 1100 (br.s) (C–O str.), 990m, 950m, 800s, 670m (C–H def.) cm^{-1}. ^{1}H NMR (neat liquid, 90 MHz,

Me_4Si ext. ref.) δ 0.3 (t, 2H, *J* 7 Hz, CH_2-Si), 1.34 (t, 9H, CH_3-CH_2), 2.0 (m, 2H, -CH_2), 2.5 (m, 2H, CH_2-ring) 3.2 (s, 9H, CH_3O-Si), 3.45 (q, 6H, *J* 8 Hz, O-CH_2), 6.0 (br s, 4H, C_5H_4) ppm.

Preparation of [η^5-(trimethoxysilylpropyl)cyclopentadienyl]trichlorotitanium(IV)

(a) From [η^5-(trimethoxysilylpropyl)cyclopentadienyl]triethoxytitanium(IV). To a solution of titanium complex (26.65 g, 65 mmol) in chloroform (20 cm^3) cooled at 0°C was added dropwise with stirring acetyl chloride (15.3 g, 195 mmol, 13.9 cm^3). Stirring was continued at 0°C for 3 h and the colour was observed to change from pale pink to deep red. After stirring for a further 12 h at room temperature, the solvent was removed to give a deep red residue. This was extracted with diethyl ether (3 × 100 cm^3), and the extract was filtered, before removal of the solvent to give compound **6** (21.0 g, 55 mmol, 85%), as an air and moisture sensitive red oil. IR (neat liquid): ν 3110 (C–H str), 2950s, 2850s (C–H str.), 1500m (C–C str), 1460 (C–H def.), 1405m, 1370m, 1340m, 1260m, 1200m (C–H def), 1090s (C–O str), 820 br. s, 760s, 665m (C–H def.) cm^{-1}. The compound turned green over 3 h in a dry box at room temperature.

(b) From tetrachlorotitanium(IV). A solution of sodium(trimethoxysilylpropyl)cyclopentadienide (43 mmol) in tetrahydrofuran was added dropwise to titanium tetrachloride (7.98 g, 42 mmol) in tetrahydrofuran (60 cm^3) at −60°C. The mixture was then stirred at −20°C for 2 h and then at room temperature for 12 h, before removal of the solvent to give a red oil. This was extracted with dry chloroform (3 × 100 cm^3) and the extract was filtered, before removal of the solvent to give **6** (4.0 g, 10 mmol) which had an identical IR spectrum to that isolated in the previous experiment, and showed the same sensitivity to air and moisture.

Attempted preparation of [η^5-(trimethoxysilylpropyl)cyclopentadienyl](η^5-cyclopentadienyl)dichlorotitanium(IV)

(a) From [η^5-$(MeO)_3Si(CH_2)_3C_5H_4$]$TiCl_3$. Sodium cyclopentadienide (17 mmol) in tetrahydrofuran (200 cm^3) was added dropwise to crude [η^5-$(MeO)_3Si(CH_2)_3$ C_5H_4]$TiCl_3$ (4.0 g, 10 mmol) in tetrahydrofuran (60 cm^3) at −10°C. The mixture was then stirred at room temperature for 12 h before removal of the solvent, and extraction of the residue with a mixture of hexane and dichloromethane (1/1 v/v). After filtration, the solvents were removed from the extract to give red crystals of bis(η^5-cyclopentadienyl)dichlorotitanium (2.98 g, 12 mmol).

(b) From (η^5-C_5H_5)$TiCl_3$. Sodium [η^5-(trimethoxysilylpropyl)cyclopentadienide] (4.3 mmol) in tetrahydrofuran (100 cm^3) was added dropwise to a solution of (η^5-cyclopentadienyl)trichlorotitanium (8.9 g, 41 mmol) in the same solvent at −30°C. The mixture was then stirred at room temperature for 16 h, before removal of the solvent, extraction of the residue with dichloromethane (2 × 100 cm^3), and removal of the solvent from the extract to give bis(η^5-cyclopentadienyl)dichlorotitanium (5.47 g, 22.0 mmol).

Preparation of SIL-$CH_2CH_2CH_2C_5H_4$Rh(COD)

Silica-gel (60–120 mesh) (5 g) was dried at 300°C for 5 h, then heated at 80°C under vacuum (0.1 mmHg) for a further 8 h. The silica was cooled under a stream of dry nitrogen, then added to 100 cm^3 of degassed, dry toluene, which had been stirred with aqueous sodium hydroxide solution (0.1 *M*, 0.1 cm^3), and the mixture was stirred at 80°C for 1 h to equilibrate. [η^5-(trimethoxysilylpropyl)cyclopentadienyl]cyclooctadienerhodium (1.14 g, 2.8 mmol) was then added and the solution was stirred at 80°C for 4 h. The solvent was decanted and the silica was washed thoroughly with diethyl ether, before transferring to a Soxhlet thimble and extracted with 1/1 dichloromethane/diethyl ether for 8 h. The silica was then dried in a vacuum drying pistol at 80°C/0.1 mmHg for 8 h to give the supported complex (6.05 g) as a pale orange solid, which rapidly turned bright green on exposure to air.

Preparation of $SIL\text{-}CH_2CH_2CH_2C_5H_4)_2TiCl_2$

Silica gel [Grace Davison 952, surface area (BET N_2) 281 m^2 g^{-1}] was dried at 300°C for 12 h, and then cooled in a stream of nitrogen, before adding to degassed toluene (100 cm^3) which had been stirred with aqueous sodium hydroxide (0.1 *M*, 0.1 cm^3). The silica was then stirred at 80°C for 1 h to equilibrate, filtered, washed several times with toluene, and dried at 300°C immediately before use.

A solution of complex **5** in toluene was stirred with the silica at room temperature for 36 h. The silica was then filtered, washed with diethyl ether, extracted with hot benzene, and dried in vacuo at 50°C.

Hydrogenation reactions

Butyllithium (1.6 *M* solution in hexane) was injected into a suspension of the supported titanium catalyst in toluene (10 cm^3) under an atmosphere of dry hydrogen, and there was a change in the colour of the silica from red to green to blue. The alkene (2 cm^3) was then injected into the mixture, and the hydrogen uptake was measured as a function of time using a gas burette (100 cm^3).

Cyclotrimerization of dimethylacetylenedicarboxylate

The acetylene (1.42 g, 10.0 mmol) in toluene (10 cm^3) was added under nitrogen to ($SIL\text{-}CH_2CH_2CH_2C_5H_4$)Rh(COD) (5.0 g) and the mixture was heated under reflux until GLC analysis confirmed the complete disappearance of the acetylene (4 h). The brick red silica-supported catalyst was then removed by filtration, and evaporation of the solvent gave hexacarbomethoxybenzene (0.34 g, 0.82 mmol, 82%).

In a kinetic study of this reaction the disappearance of DMAD was monitored by GLC (Pye-Unicam 104 with flame ionisation detector; 1.2 m OV 1 column; Hewlett Packard 3352 B integrator) using dimethyldigol as internal standard. DMAD (1.69 g, 7.0 mmol), and dimethyldigol (0.94 g, 7.0 mmol) were added via a syringe to a mixture of the catalyst (2 g) in toluene (10 cm^3) heated at reflux temperature. Samples (0.2 cm^3) were removed at 30 min intervals and the acetylene concentration was calculated from the ratios of the areas of dimethyldigol/acetylene. A good straight line-plot of $\ln(a/a-x)$ vs. time was obtained for at least 95% conversion, with a standard error in the range of 2–4%.

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