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THE ROLE OF THE TRANSITION METAL IN THE HOMOGENEOUS CATALYTIC POLYMERISATION OF STRAINED ORGANOSILICON HETEROCYCLES

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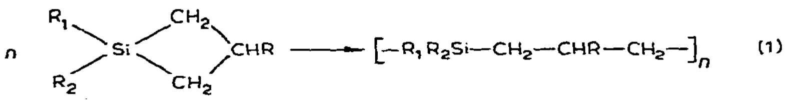
SUMMARY

A number of transition metal complexes have been examined as catalysts for the polymerisation of silacyclobutanes $R(X)\overline{SiCH_2CH_2CH_2}$($R=X=CH_3$ or OCH_3; or $R=CH_3$ and $X=Cl$). Active complexes include $(C_2H_4PtCl_2)_2$, $[(CO)_2RhCl]_2$, $[(C_6H_5)_3P]_3RhCl$ and $[(C_6H_5)_3P]_3RhCH_3$, whereas the following are relatively inactive: $[(C_6H_5)_3P]_2Rh(C_6H_4PPh_2)$, $[(C_6H_5)_3P]_4RhH$, $[(C_6H_5)_3P]_2PtCl_2$, $[(C_6H_5)_3P]_2Ir(CO)Cl$, and $[(CH_3)_3SiCH_2]_4Zr$. A mechanism is suggested which involves successively: (*a*) insertion of the transition metal M into a Si–C bond (ring expansion of the SiC_3 ring by oxidative addition to the transition metal), (*b*) formation of a linear M–alkyl by halogen or alkyl transfer from M to Si (ring opening), (*c*) propagation by repeated combination of (*a*) and (*b*) and (*d*) chain termination by β-hydrogen abstraction or alkane elimination. Evidence is provided by product isolation and by approximate rate measurements.

INTRODUCTION

Strained organosilicon heterocycles such as silacyclobutanes, 1,3-disilacyclobutanes, and 2,3-benzo-1-silacyclobutenes are important as precursors of organosilicon polymers having a silicon–carbon backbone[1,2], *e.g.*, as in eqn. (1):



Polymerisation may be induced by heating, but there have been a number of studies in which transition metal catalysts have been employed[3–6], the reactions proceeding similarly but at lower temperatures. Some catalysts are so effective that polymerisation occurs upon mixing at room temperature[5,6]. (Such transformations form an interesting contrast to the transition metal-promoted valence isomerisation of strained carbocyclics[7].) A mechanism involving siliconium ions has been proposed for the polymerisation of 1,3-disilacyclobutanes by transition metal salts ($PtCl_2$, $PdCl_2$, RuI_3, $PtCl_6^{2-}$, $IrCl_6^{2-}$, $RuCl_6^{2-}$, or $AuCl_4^-$) in which the role of the catalyst was not specifically defined [see eqn. (2), $R = CH_3, C_6H_5, C_2H_5O, Cl$][6]:

$$\begin{tikzcd}
{[R(CH_3)SiCH_2]_2} \arrow[r, shift left, "\text{catalyst}"] & R(CH_3)\overset{+}{Si}CH_2(R)CH_3Si\overset{-}{C}H_2 \arrow[l, shift left] \arrow[r, "{[R(CH_3)SiCH_2]_2}", "\text{or dimerization}"'] & {}
\end{tikzcd}$$

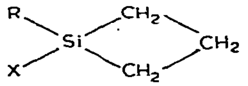
$$\begin{tikzcd}
\longrightarrow \overset{-}{C}H_2[R(CH_3)SiCH_2]_3 \arrow[d] & (R)CH_3\overset{+}{Si} \arrow[d, "\text{etc}"] \\
{[R(CH_3)SiCH_2]_4} & \text{polymer}
\end{tikzcd} \qquad (2)$$

A radical mechanism was considered unlikely[6]. Later workers have agreed with these proposals and have suggested extensions to the zwitterionic mechanism[4].

We now report studies on the polymerisation of a number of 1,1-disubstituted silacyclobutanes by neutral transition metal complexes in benzene solution which clarify the role of the catalysts under these conditions.

EXPERIMENTAL

The transition metal compounds studied are designated (I)–(IX) and the silacyclobutanes (A)–(C) as follows. They were prepared by published methods, except where otherwise stated.



$R{=}X{=}CH_3$[1] : (A)
$R{=}X{=}OCH_3$* : (B)
$R{=}CH_3, X{=}Cl$[1] : (C)

$[C_2H_4PtCl_2]_2$[8]	(I)
$[(CO)_2RhCl]_2$[9]	(II)
$[(C_6H_5)_3P]_3RhCl$[10]	(III)
$[(C_6H_5)_3P]_3RhCH_3$[11]	(IV)
$[(C_6H_5)_3P]_2Rh[C_6H_4P(C_6H_5)_2]$[11]	(V)
$[(C_6H_5)_3P]_4RhH$[12]	(VI)
$[(C_6H_5)_3P]_2PtCl_2$[13]	(VII)
$[(C_6H_5)_3P]_2Ir(CO)Cl$[14]	(VIII)
$[(CH_3)_3SiCH_2]_4Zr$[15]	(IX)

All reactions were carried out in benzene under nitrogen at 21°. Infrared spectra (4000–250 cm^{-1}) of metal complexes were recorded as Nujol mulls on a Perkin–Elmer 457 spectrometer. Concentrations refer to mononuclear transition metal units, *i.e.*, (I) and (II) are considered as $[L_2MCl]$.

Determination of relative catalytic activity

Polymerisation reactions were followed by observing the rate of disappearance of the RSi PMR signal (Varian Associates T60 spectrometer, probe temperature 34°, internal reference C_6H_6 $\tau 2.73$) since this was a sharp singlet (CH_3 or OCH_3) and resonances due to the polymer appeared as broad multiplets under these conditions. The validity of this treatment was established by making parallel GLC measurements in one case: viz. polymerisation of (A) with 83% mol equiv. (I), in bromobenzene as solvent.

1. To a solution of the appropriate metal complex (I)–(III) (2.7 μmol) in benzene (0.50 ml) was added the silacyclobutane (27 μmol), the ensuing reaction being followed by PMR spectroscopy. With (IV), the silacyclobutane (27 μmol) in benzene

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* Gift from Dow Corning, Limited (Barry).

(0.50 ml) was added to the solid Rh complex (2.7 μmol) to give a homogeneous solution which was studied similarly.

2. To a solution [(V) or (IX)] or suspension [(VI), (VII), or (VIII)] of the metal complex (54 μmol) in benzene (1.00 ml) was added the silacyclobutane (54 μmol) and the mixture was stirred for 24 h. A portion (0.50 ml) of clear [except (VII)] solution was then decanted and its PMR spectrum compared with that of a standard sample (27 μmol silacyclobutane in 0.50 ml C_6H_6). With complexes (VII) and (IX), solvent and unchanged silacyclobutane were then distilled *in vacuo* and the spectrum of the distillate recorded to confirm the yield of unchanged monomer.

Examination of transition metal products

In all the following cases, the homogeneous solutions showed only polymer PMR resonances for the silicon residue.

1. Addition of (A) (40 mg, 0.40 mmol) to a stirred suspension of (I) (98 mg, 0.33 mmol) in benzene (5.0 ml) caused rapid (within minutes) polymerisation of the silacyclobutane, the resulting yellow homogeneous solution gradually (hours) darkening and becoming heterogeneous. Removal of solvent gave an intractable gum. Introduction of ligand [$(C_6H_5)_3P$, $(C_6H_5)_2CH_3P$, or 4-picoline, 0.67 mmol; or 2,2'-bipyridine, 0.33 mmol to the yellow solution did not yield (fractional crystallisation) a tractable platinum–silicon derivative. In the $(C_6H_5)_3P$ reaction, *trans*-$[(C_6H_5)_3P]_2PtHCl$[16] (ca. 3 mg) was obtained in addition to *cis*-$[(C_6H_5)_3P]_2PtCl_2$ and unchanged $(C_6H_5)_3P$ (IR spectroscopic identification). The reaction of (B) with (I) was similar but faster. Treatment of (I) (24.5 mg, 0.083 mmol) in benzene (2.0 ml) with n-C_4H_9Li (0.083 mmol) in hexane solution (84 μl) caused instant and complete decomposition to dark insoluble material.

2. Addition of (A) (40 mg, 0.40 mmol) to a stirred solution of (II) (65 mg, 0.33 mmol) in benzene (5.0 ml) caused the yellow solution to darken rapidly and deposit a solid. Introduction of $(C_6H_5)_2CH_3P$ (134 mg, 0.67 mmol) at an early stage gave a silicon-free material. Enhanced reactivity of (B) with (II) was noted.

3. Addition of (A) (67 mg, 0.67 mmol) to a stirred suspension of (III) (308 mg, 0.333 mmol) in benzene (5.0 ml) gave a thermally-stable deep orange solution after 3 h. Volatile material was removed *in vacuo* and combined with the hexane washings of the orange-yellow residue. Treatment of the combined solution with 0.1 *M* NaOH (10.00 ml) gave a bulky precipitate of siloxane-crosslinked polymer. Back-titration of the separated aqueous layer with 0.1 *M* HCl indicated 0.278 mmol hydrolysable chloride (84%). The IR spectrum of the orange-yellow rhodium residue showed it to consist largely of $[(C_6H_5)_3P]_2Rh[C_6H_4P(C_6H_5)_2]$ (V) together with some hydridic [ν(Rh–H) 2150 cm^{-1}] material closely resembling $[(C_6H_5)_3P]_4RhH$ (VI) [ν(Rh–H) 2150 cm^{-1}] in its IR absorptions. In similar experiments with (B) and (C) (0.333 mmol) and (III) (0.333 mmol) the silacyclobutanes were polymerised (PMR) and the reaction mixtures were not examined further.

4. A saturated (0.0280 *M*) solution of (IV) in benzene at 6° was divided between two PMR tubes, one being previously empty and the other containing (A) (2 molar equivalents). The tubes were placed in the PMR machine at 34°. The Rh–CH_3 resonance (τ9.46) of complex (IV) in the presence of (A) was barely detectable after 5 min and absent after 15 min, whereas the signal from the control sample could still be seen at reduced (to ca. 25%) intensity [(IV)→(V)+CH_4] after 30 min.

RESULTS

1. Reactions between (A) and complexes (I)–(IV) (10 mol %) showed these compounds to be active catalysts under our conditions (which are arbitrary and not intended to represent optima). The general form of the monomer decay curve is represented schematically in Fig. 1. Times $t(x)$ for polymerisation of $x\%$ monomer were:

t(25%): (I) 0.5; (II) 1.5; (III) 0.5; (IV) 2.0 h
t(50%): (I) 1.9; (II) 68.0; (III) 4.3; (IV) 12.7 h

2. In reactions involving (A) [concentration as in (*1*)] but with an equimolar proportion of complexes (V)–(IX), the following amounts of (A) remained after 24 h: (V) (stirred solution), 34%; (VI) (stirred suspension), 74%; (VII) (stirred suspension), 96%; (VIII) (stirred suspension), 100%; (IX) (stirred solution), 100%. Thus, these compounds are relatively inactive.

3. Under stoichiometric conditions (A) reacts with sparingly-soluble (I) to afford benzene soluble material; the solution is unstable; addition of $(C_6H_5)_3P$ gives some *trans*-$[(C_6H_5)_3P]_2PtHCl$.

4. Similarly, (A) reacts with (III) to give (V) and $[(C_6H_5)_3P]_3(L)RhH$ [L = $(C_6H_5)_3P$ or solvent]. Chlorine is transferred from rhodium to silicon. Complexes (III) and (IV) show similar catalytic activity, although (IV) contains no halogen.

5. The rate of disappearance of the Rh–CH_3 PMR signal of (IV) in the presence of (A) is markedly greater than that due to the decomposition of (IV) in solution [(IV)→(V)+CH_4].

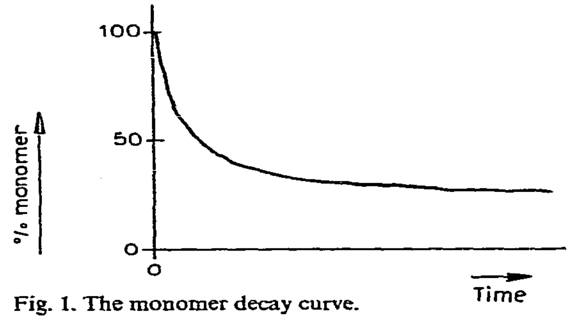


Fig. 1. The monomer decay curve.

DISCUSSION

On the basis of the studies described above, we suggest a polymerisation mechanism involving the following steps (see also Fig. 2). This has some similarity to mechanisms proposed[17] for olefin polymerisation by Ziegler-type catalysts, but differs in the initial oxidative addition step.

(*a*). Oxidative addition of the silacyclobutane to the transition metal complex (ring expansion).

(*b*). Formation of a linear transition metal–alkyl by halogen (or alkyl) transfer from the metal to silicon (ring opening).

(*c*). Polymer growth by insertion of further co-ordinated silacyclobutane into the linear metal–alkyl.

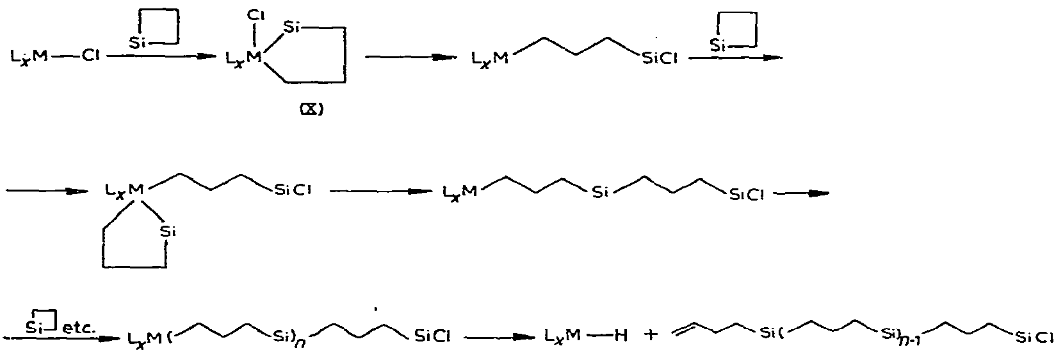
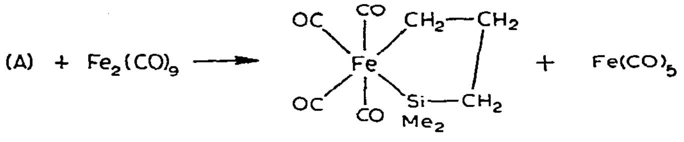


Fig. 2. Schematic representation of silacyclobutane polymerisation.

(*d*) Chain termination by β-hydrogen abstraction or (possibly) homolytic metal–alkyl bond fission or [exceptionally, with (III)] by alkane elimination.

Of major importance to the mechanism are the intermediates such as (X) (see Fig. 2) in which insertion of a transition metal into a silacyclobutane [step (*a*)] has taken place. Although we were unable to isolate such a complex from polymerisation reactions, even when silacyclobutanes (B) and (C) carrying electronegative substituents at silicon were used, we succeeded in synthesising a model compound (XI)[18] from a system in which no further ring-opening (and subsequent polymerisation) could occur.



(XI)

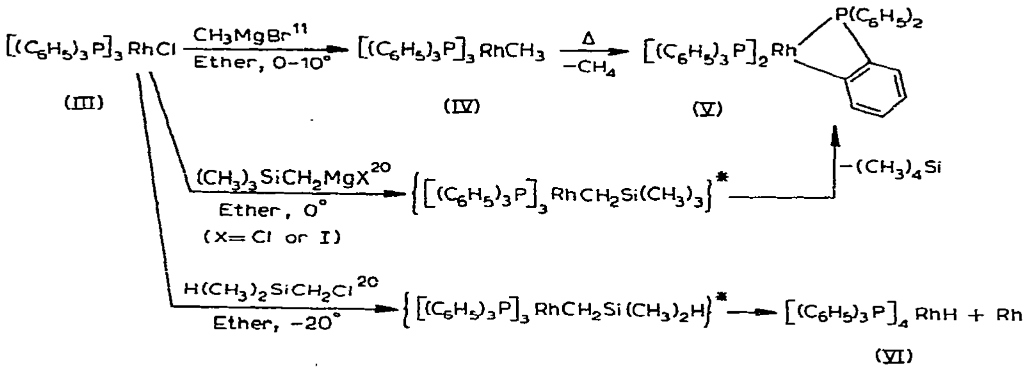
The complex (XI) is notable in the present context for its reactions with neutral ligands (L) to form $L_xFe(CO)_{5-x}$ ($x = 1, 2$) and organosilicon polymers.

Evidence for step (*b*) rests largely on the demonstration that in the reaction between (A) and (III) chlorine is transferred from Rh to Si, and also on the comparison of activities between the rhodium chloride (III) and the alkylrhodium (IV). Consistent with the proposed insertion step (*c*) is the observed increase in the rate of disappearance of the Rh–CH_3 PMR signal of (IV) when (A) is present.

Step (*d*) is supported by the isolation of hydrido transition metal complexes of Pt and Rh and by the isolation of the Rh complex (V). Relevant to the argument are the known reactions shown in Scheme 1.

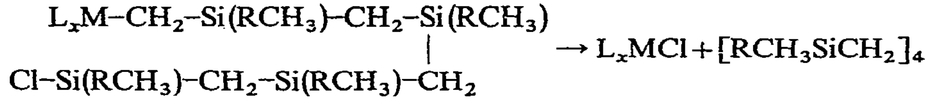
Although, from the mechanism suggested, it might be expected that (III) and (IV) should show very similar catalytic activity, the results indicate that (IV) is a somewhat poorer catalyst than (III). However, this apparent discrepancy is readily explained by the facile decay of (IV) into (V) (a relatively inactive compound) in solution. Hence, even though the solution of (A) was added to solid (IV) to minimise this, the effective concentration of (IV) suffered some reduction. The NMR experiment (above) gives a guide to the relative rates of the competing reactions. The sharp decline in activity observed for (II) is due to the rapid reduction of this complex to insoluble material.

$$trans\text{-}[(C_2H_5)_3P]_2Pt(C_2H_5)Cl \xrightarrow[-C_2H_4]{\Delta} trans\text{-}[(C_2H_5)_3P]_2PtHCl^{19}$$



The lack of catalytic activity found for the zirconium tetraalkyl (IX), which is an effective α-olefin polymerisation catalyst[21], is consistent with the proposed mechanism, since a Zr^{VI} intermediate would be required. It is clear that an effective transition metal catalyst must be co-ordinatively unsaturated and in low oxidation state, and must possess a mobile ligand such as Hal^- or R^- which is capable of migrating from the transition metal to silicon.

In the study of 1,3-disilacyclobutane polymerisation[6] referred to earlier (see Introduction), isolation of small quantities of the cyclic compound $[R(CH_3)SiCH_2]_4$ was rationalised through the postulated ionic mechanism[6]. The formation of this product could also be explained in terms of a modification of the mechanistic scheme outlined in Fig. 2 and discussed above. In this modification, when the length of the silylmethylene chain attached to the metal is sufficient, ring-closure could occur in an overall process represented as follows:



$$\begin{array}{ll} L_xM\text{–}CH_2\text{–}Si(RCH_3)\text{–}CH_2\text{–}Si(RCH_3) & \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | & \rightarrow L_xMCl + [RCH_3SiCH_2]_4 \\ Cl\text{–}Si(RCH_3)\text{–}CH_2\text{–}Si(RCH_3)\text{–}CH_2 & \end{array}$$

The ring closure might possibly involve oxidative-addition of the Si–Cl link to the transition metal atom, followed by formation of a bond between the $-CH_2-$ and $Si(RCH_3)-$ centres attached to the metal; the latter process would be analogous to the final step of hydrosilylation of olefins catalysed by platinum complexes, in which a silyl group and a primary alkyl group are thought to separate in combination from the metal. Direct oxidative-addition of a Si–Cl bond to the metal is not essential; exchange between Si–Cl and Si–H or Pt–H present in catalytic amounts could first occur to give a terminal $HSi(RCH_3)-CH_2-$ grouping, and the well-established oxidative-addition of a silicon hydride to the metal would follow.

The formation of telomers[3,5], *e.g.* $R'_3Si[CH_2CH_2CH_2SiR_2]_xH$, from mixtures of trialkylsilane R'_3SiH and silacyclobutane $R_2\overline{SiCH_2CH_2CH_2}$ species can also be readily understood in the terms of an analogous process, as follows:

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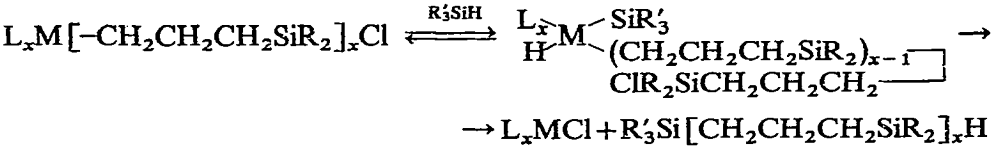
* Not isolated.



$$L_xM[-CH_2CH_2CH_2SiR_2]_xCl \xrightleftharpoons{R'_3SiH} \begin{matrix} L_x & & SiR'_3 \\ & M & (CH_2CH_2CH_2SiR_2)_{x-1} \\ H & & ClR_2SiCH_2CH_2CH_2 \end{matrix} \rightarrow$$

$$\rightarrow L_xMCl + R'_3Si[CH_2CH_2CH_2SiR_2]_xH$$

Once again, SiCl/Si–H exchange might be involved.

ACKNOWLEDGEMENT

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