Organolanthanide-catalysed Oligomerisation of 2-Cycloalken-1-ones

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Yttrium and lanthanum hydrides $[(C_5Me_5)_2LnH]_2$ are active catalysts for the oligomerisation of 2-cycloalken-1-ones; the average degree of oligomerisation increases with temperature.

Group 3 hydrides $[(\eta^5\text{-}C_5Me_5)_2LnH]_2$ **1** (Ln = Y **1a**, La **1b**) are effective catalysts for the polymerisation of α-olefins.[1,2] The presence of C–X functions (X = heteroatom) in the substrate usually leads to rapid formation of Ln–X bonds and results in deactivation of the catalyst. Recently, however, examples have been reported on organolanthanide-catalysed polymerisation of functionalised monomers, *e.g.* living polymerisation of methyl methacrylate (MMA)[3] producing high molecular weight polymers with narrow molecular weight distributions. Here we report the catalytic oligomerisation of cyclic α,β-unsaturated ketones, an observation which opens up interesting opportunities for the synthesis of functionalised (co)polymers.[4]

Complexes **1a** and **1b** proved to be active catalysts for the oligomerisation ($P_n \leq 15$) of 2-cyclopenten-1-one (Table 1).† To rule out thermally induced oligomerisation, experiments were conducted without a precatalyst (100 °C for 24 h), but left only unreacted monomer. The stability and robustness of the catalyst is demonstrated by the observation that the oligomerisation started again upon addition of new monomer after the original amount had been consumed. The newly formed oligomers appeared to be identical with those of the initial process.

Table 1 Catalytic oligomerisation of 2-cyclopenten-1-one

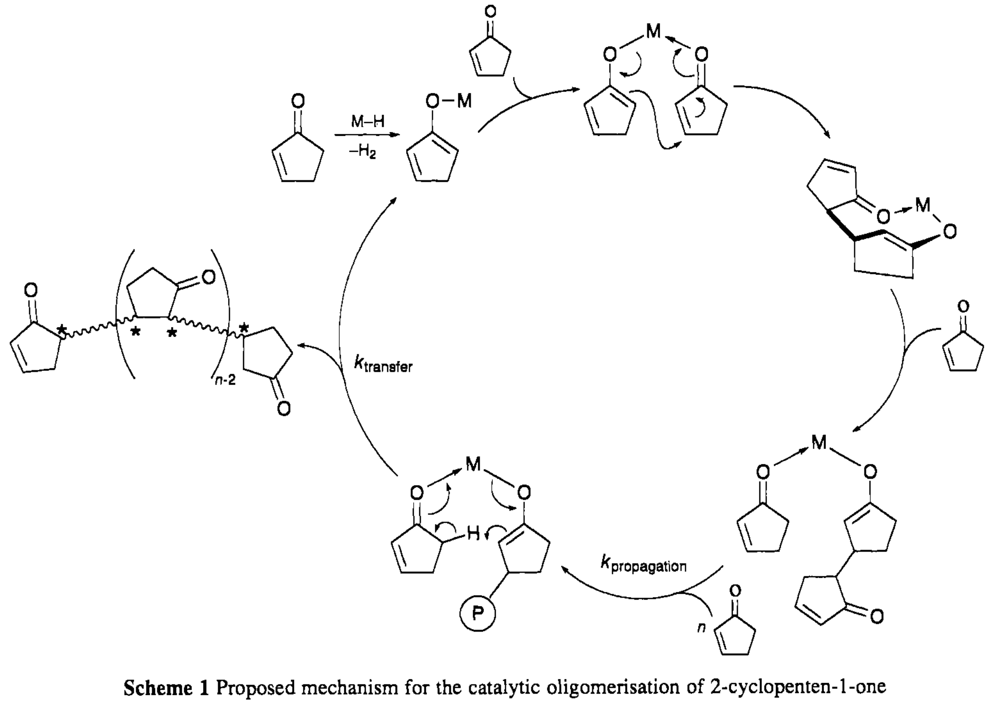
Entry	Precatalyst	Temp./°C	P_n[a]
1	**1a**	25	3.5
2	**1a**	50	5.3
3	**1a**	75	9.9
4	**1a**	100	15
5	**1b**	25	2.7
6	**1b**	50	3.6
7	**1b**	100	4.8

[a] Average degree of oligomerisation (P_n) determined by dividing M_n (VPO) by the molecular weight of the monomer.

For a number of catalytic runs, the turnover frequency was determined and it was found that complex **1b** showed a higher activity (≥150 mmol consumed monomer per mol precatalyst per hour at 25 °C) than **1a** (activity ≤100 h^{-1}). This difference may reflect the larger ionic radius of lanthanum and is in line with the observations for the polymerisation of ethene[1] and MMA.[3] Precatalyst **1a** produces higher molecular weight oligomers, suggesting a less favourable chain transfer compared to **1b**.

The oligomers contain both α,β-unsaturated carbonyl groups with a disubstituted olefinic moiety and non-conjugated carbonyl groups, as was concluded from IR and NMR spectroscopy. The original ring structure of the monomer appears to be intact (FAB- and FD-MS). Since the intensity of the olefinic resonances in the ^1H NMR spectrum decreases proportionally with increasing P_n, it is likely that an α,β-unsaturated carbonyl group is one of the oligomer end groups. A possible oligomer structure is depicted in Scheme 1. Apparently, the oligomers have an atactic microstructure, which can be deduced from multiple resonances in the carbonyl region of the ^{13}C NMR spectra. Stereoselective oligomerisation using chiral organolanthanide complexes, which could simplify the mixture, has not been attempted thus far.

The α,β-unsaturated carbonyl end group most likely originates from an initiation step in which hydrogen is abstracted from the monomer at the kinetically favoured α-position.[5] The resulting enolate attacks another monomer at the 3-position (1,4-addition) to form a new C–C bond and generate another enolate. Subsequent monomer complexation and 1,4-addition produces oligomers, similar to the organolanthanide-catalysed



Scheme 1 Proposed mechanism for the catalytic oligomerisation of 2-cyclopenten-1-one

polymerisation of MMA.[3] Chain transfer can follow through hydrogen abstraction at the α-position of the incoming monomer forming the oligomer and regenerating the catalytically active enolate species (Scheme 1).

The unusual temperature effect observed for the catalytic oligomerisation of 2-cyclopenten-1-one is remarkable (Table 1): at room temperature small oligomers have been produced, while P_n increases at higher reaction temperature. To check the possibility that small oligomers like those formed at low temperature enter oligomerisation at higher temperature, the following experiment was performed. The reaction mixture resulting from oligomerisation at 25 °C (Table 1, entry 1) was heated to 100 °C. An orange insoluble product resulted, totally different in nature compared to that obtained from **1a** and pure monomer at 100 °C.‡ Therefore, we can exclude a mechanism in which low molecular weight oligomers formed at low temperature couple at higher temperatures. A simple mechanism involving chain propagation by 1,4-addition and chain termination by hydrogen transfer from the monomer seems to be more plausible.

Assuming the mechanism mentioned above, the rate of propagation can be described as $v_p = k_p[M][Cat^*]$ and the chain transfer rate $v_{tr} = k_{tr}[M][Cat^*]$. The oligomerisation degree is determined by $P_n = k_p/k_{tr}$, which allows the differences in activation parameters to be estimated from an Eyring plot (Fig. 1): $\ln P_n = (\Delta G^{\neq}_{tr} - \Delta G^{\neq}_p)/RT = (\Delta H^{\neq}_{tr} - \Delta H^{\neq}_p)/RT - (\Delta S^{\neq}_{tr} - \Delta S^{\neq}_p)/R$.[6] The calculated $(\Delta H^{\neq}_{tr} - \Delta H^{\neq}_p)$ values are −18(1) and −7.0(9) kJ mol^{-1}, while the $(\Delta S^{\neq}_{tr} - \Delta S^{\neq}_p)$ values are −71(4) and −32(3) J mol^{-1} K^{-1} for **1a** and **1b**, respectively. Assuming positive values for $\Delta H^{\neq}_{tr}$ and $\Delta H^{\neq}_p$, it can be concluded that $\Delta H^{\neq}_{tr} < \Delta H^{\neq}_p$, which is highly unusual in early transition metal-catalysed processes. However, $\Delta G^{\neq}_{tr} > \Delta G^{\neq}_p$ for the entire temperature range studied, due to the significant difference in activation entropy between the propagation and chain transfer.

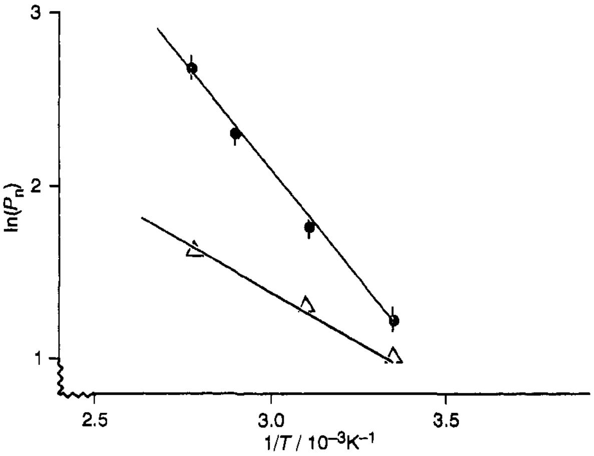


Fig. 1 Eyring plot of ln (P_n) *vs.* 1/*T* for the oligomerisation of 2-cyclopenten-1-one catalysed by **1a** (●) or **1b** (△)

Complexes **1a** and **1b** are also active catalysts for the oligomerisation of 2-cyclohexen-1-one. Both turnover frequency and P_n are lower while the temperature effect is much smaller giving a $(\Delta H_{tr} - \Delta H_p)$ value close to 0 kJ mol^{-1}.

This investigation was supported by Netherlands Foundation for the Advancement of Scientific Research (SON/NWO) (B. J. D.) and Innovative Oriented Research Programs on Catalysis (IOP-katalyse) of the Dutch Ministry of Economic Affairs (E. A. B.). We thank Dr B. Rieger (Tübingen, Germany) for FAB-MS and FD-MS measurements.

Received, 3rd April 1995; Com. 5/02090E

Footnotes

† All reactions were performed under nitrogen using standard Schlenk and glove box (Braun MB200) techniques. Solvents and 2-cycloalken-1-ones (Janssen) were distilled from Na melt and stored under nitrogen. $[(\eta^5\text{-}C_5Me_5)_2YH]_2$[7] **1a** and $[(\eta^5\text{-}C_5Me_5)_2LaH]_2$[1] **1b** were prepared according to a published procedure.

Selected spectroscopic data for the products Table 1, entry 1. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, $SiMe_4$): δ 7.61 (m, 1 H), 6.03 (m, 1 H) and multiple overlapping signals in the range 3.5–1.0 (24 H). ^{13}C- NMR (75.4 MHz, $CDCl_3$, 25 °C, $SiMe_4$): δ 218.0 (C=O), 217.0 (C=O), 197.0 (C=C–*C*=O), 163.6 (*C*=C–C=O), 163.3 (*C*=C–C=O), 163.1 (*C*=C–C=O), 134.7 (C=*C*–C=O) and 134.3 (C=*C*–C=O), multiple overlapping signals in the range δ 55–20. VPO ($CHCl_3$): M_n = 272.

‡ The product formed is presumably a highly cross-linked material resulting from thermal degradation.

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