Alkyl Bridged Complexes of the Group 3A and Lanthanoid Metals as Homogeneous Ethylene Polymerisation Catalysts

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Summary The fully characterised group 3A and lanthanoid metal complexes $[M(\eta\text{-}C_5H_4R)_2Me]_2$ (M=Y or Er, R=H, Me, or $SiMe_3$, and M=Yb, R=H or Me) and $[M(\eta\text{-}C_5H_4R)_2Me_2AlMe_2]$ (M=Y, Er, Ho, or Yb, R=H or Me, and M=Y, R=$SiMe_3$) are active homogeneous ethylene polymerisation catalysts; they show an intramolecular deactivation process involving abstraction of a cyclopentadienyl hydrogen which is completely suppressed with peralkylated derivatives.

PREVIOUSLY we have described the preparation of stable alkyls of the group 3A and lanthanoid metals $[M(\eta\text{-}C_5H_5)_2\text{-}R_2AlR_2]$ (M=Sc, Y, Gd, Dy, Ho, Er, Tm, or Yb, R=Me and M=Sc, Y, or, Ho, R=Et) and $[M(\eta\text{-}C_5H_5)_2R]_2$ (M=Y, Dy, Ho, Er, Tm, or Yb, R=Me), which interestingly were shown to have a doubly bridged structure.[1] We were intrigued as to the possibility that such compounds could serve as suitable models for Ziegler–Natta type polymerisation intermediates. Electron deficient alkyl bridged species have been postulated as intermediates in Ziegler catalysis by a variety of authors,[2] but no such species have been characterised. We now show that the two related classes of group 3A and lanthanoid metal compounds $[M(\eta\text{-}C_5H_4R)_2Me_2AlMe_2]$ and $[M(\eta\text{-}C_5H_4R)_2Me]_2$ (R=H, Me, or $SiMe_3$) are active homogeneous ethylene polymerisation catalysts.

These catalyst systems are unusual in that previous cyclopentadienyl systems were found to have little or no activity [a recent system $Ti(\eta\text{-}C_5H_5)_2Me_2\text{-}AlEt_3\text{-}H_2O$ was shown to be active; the active species was not identified[3]]. Also active halogen-free homogeneous systems from the early transition metals are rare and those based on group 3A–lanthanoid metals are unknown.

$[M(\eta\text{-}C_5H_4R)_2Me]_2$ has been studied with a variety of metals (M) and alkyl substituents (R) over a range of polymerisation conditions. Although no systematic metal effect was observed best results were obtained for M=Y or Er (Table). The cyclopentadienyl group has a marked effect on the polymerisation. For a given metal, across the series R=H, Me, and $SiMe_3$, the following trends were observed.
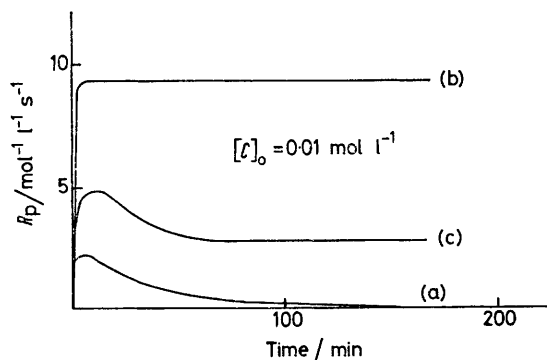
(a) The activity increases. This may be related to an increase in electron density in the bridge. Initial activities of 10—200 g mmol^{-1} atm^{-1} h^{-1} have been observed. (b) The molecular weight decreases. $\overline{M}_w/\overline{M}_n$ values of 1·5—2·5 were observed and are in the range expected for a homogeneous catalyst. The low value of $\overline{M}_n$ indicates a ready transfer reaction. (c) The catalyst lifetime decreases. Lifetime is also inversely dependent on temperature and rarely exceeds 2—3 h.

FIGURE. Rate profiles. (a) $[Er(\eta\text{-}C_5H_5)_2Me]_2$ (105 °C), (b) $[Y(\eta\text{-}C_5Me_4Et)_2Bu^n]$ (75 °C), (c) $[Y(\eta\text{-}C_5H_4SiMe_3)_2Me_2AlMe_2]$ (105 °C).

A typical rate profile is shown in the Figure (a). The first-order deactivation process involves H-abstraction from a cyclopentadienyl group adjacent to the propagating centre. Similar behaviour has been noted in the thermolysis of the model compounds $[Y(\eta\text{-}C_5H_4R^1)_2R^2]_2$ {R^2= n-C_4H_9 or n-C_8H_{17}; prepared from $[Y(\eta\text{-}C_5H_4R^1)_2Cl]$ and R^2Li} (Scheme 1).

The ^{13}C n.m.r. spectrum of (2) shows a complex cyclopentadienyl region. The $\eta^5\text{-}C_5H_4Me$ ring carbons are shifted downfield (ref. $SiMe_4$) [112·2, 116·6, and 121·9 p.p.m.; *c.f.* (1) 109·7, 112·9, and 120·2 p.p.m.] and the methyl carbon atom resonates at 15·1 p.p.m. [*cf.* (1) 15·9 p.p.m.]. The bridging cyclopentadienyl resonance is

TABLE. Polymerisation data

| Compound	Temp/°C	Initial activity (g mmol^{-1} atm^{-1} h^{-1})	Lifetime/min	$\overline{M}_n \times 10^3$	D
$[Er(\eta\text{-}C_5H_5)_2Me]_2$	100	10·3	100	14	2·3
$[Er(\eta\text{-}C_5H_4Me)_2Me]_2$	100	27·1	94	4·7	2·5
$[Er(\eta\text{-}C_5H_4SiMe_3)_2Me]_2$	100	82·3	72	1·5	2·5
	70	25·6	190	4·1	2·6
$[Y(\eta\text{-}C_5H_4SiMe_3)_2Me]_2$	100	16·6	52	2·1	2·1
	70	5·2	155	10·5	2·5
$[Er(\eta\text{-}C_5H_4SiMe_3)_2Bu^n]_2$	100	22·4	40	6·1	1·8
$[Y(\eta\text{-}C_5H_4SiMe_3)_2Me_2AlMe_2]$	100	23·8	>>200	1·7	1·5
$[Y(\eta\text{-}C_5Me_4Et)_2Bu^n]$	75	42·3	>>200	6·8	2·74
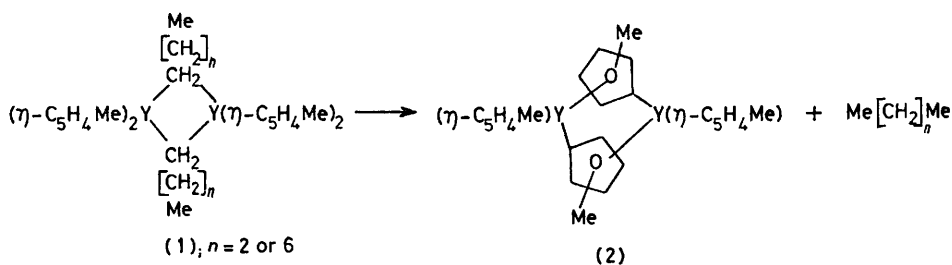
SCHEME 1

complex owing to different isomeric forms depending on which hydrogen is abstracted (ring carbons 109—113 p.p.m., complex; and provisional assignments Y–C 29·5 and 30·9 p.p.m. and the methyl substituent 15·8 p.p.m., broad). The butane or octane was detected by g.l.c.–mass spectrometry. No alkene was observed indicating that β-hydrogen elimination was absent. The reactive nature of cyclopentadienyl groups is well established in the chemistry of titanocene and its derivatives[4] and recently a hydrogen abstraction reaction has been reported during the thermal decomposition of $[Th(\eta-C_5H_5)_3Bu^n]$.[5] By using a fully substituted cyclopentadienyl group, C_5Me_4Et, the hydrogen abstraction deactivation process can be eliminated and these catalysts have enhanced lifetimes [Figure (b)].

The precise nature of the monomer insertion step is not fully defined. Insertion could go via either (a) the dimeric $[(\eta-C_5H_4R^1)_2MR^2_2M(\eta-C_5H_4R^1)_2]$ or (b) the monomeric $[(\eta-C_5H_4R^1)_2MR^2]$. The isolation of the intermediate model compounds $[Y(\eta-C_5H_4Me)_2Bu^n]_2$ [^{13}C n.m.r. spectrum: YC_2Y 38·7 p.p.m., t, $^1J(^{89}Y-C)$ 22·8 Hz] and $[Y(\eta-C_5H_4Me)_2(n-C_8H_{17})]_2$ [^{13}C n.m.r. spectrum: YC_2Y 39·3 p.p.m., t, $^1J(^{89}Y-C)$ 23·0 Hz; ^{1}H n.m.r. spectrum: $\overline{YCH_2YCH_2}$ τ10·2, 9 line m] supports the formulation of the polymerisation intermediate retaining the double alkyl bridged structure. The model studies, by ^{1}H or ^{13}C n.m.r. spectroscopy, show that the dimer is the predominant form of the catalyst at the polymerisation temperature. However, a low concentration of the potentially active monomeric species, undetectable by n.m.r. spectroscopy, cannot be ruled out. If $[Y(\eta-C_5H_4Me)_2Me]_2$ and $[Y(\eta-C_5H_4Me)_2Bu^n]_2$ are mixed together rapid scrambling of the bridge groups is observed and suggests a monomer–dimer equilibrium.

The related aluminium containing complexes $[M(\eta-C_5H_4R)_2Me_2AlMe_2]$ are also active polymerisation catalysts but exhibit a threshold effect. $[Y(\eta-C_5H_5)_2Me_2AlMe_2]$ was found to be inactive at 75 °C and 5 bar,[6] conditions under which the homometallic systems are active. Raising the temperature to ≥95 °C or markedly increasing the ethylene pressure to 33 bar initiates polymerisation. Trace im-

purities have a profound but not always deleterious effect on the activity of these compounds. Additives such as air or a Lewis base generally lower the thermal threshold for polymerisation probably owing to formation of the homometallic species.[1] A typical rate profile [Figure (c)] shows that for the aluminium systems the deactivation process does not go to completion. The second cyclopentadienyl ring is not accessible for hydrogen abstraction and the remaining alkyl group is available as a polymerisation centre (Scheme 2).

SCHEME 2
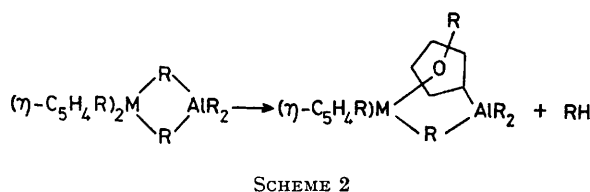
It is evident that these compounds give new information about the type of structural intermediates which may be encountered in Ziegler–Natta systems. In addition, we draw attention to the closely related complexes $[M(\eta-C_5H_4R^1)_2R^2]_2$ and $[M(\eta-C_5H_4R^1)_2Me_2AlMe_2]$, the former being free of co-catalyst and the latter containing co-catalyst residues (co-ordinated $AlMe_3$). These are the first examples of their type. That both systems produce active catalysts gives support to the ideas that the co-catalyst species, in Ziegler–Natta catalysts, serve both to alkylate M–Cl and to stabilise, via alkyl bridges, co-ordinatively unsaturated active centres (cf. the greater thermal stability and enhanced catalyst lifetime of the latter complexes over the former).

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