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New homogeneous ethylene polymerization catalysts derived from transition metal imido precursors

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SUMMARY

New ethylene polymerization catalysts based on half-sandwich imido complexes of the Group 5 metals and bis(imido) complexes of the Group 6 metals are described.

INTRODUCTION

The discovery in the early 1980's that methylalumoxane (MAO) dramatically enhances the activity and longevity of Group 4 metallocene-based olefin polymerization catalysts (1), and the subsequent advances that have been made towards well-defined, single-component systems (2), have stimulated intense academic and industrial interest in metallocene-based polymerization technology. An important challenge lies in extending this type of chemistry to other transition metal systems, where modified activities and selectivities, particularly with regard to co-monomer incorporation and increased tolerance of heteroatom functionalities, may result.

The substitution of a mono-anionic cyclopentadienyl (Cp) ring in a Group 4 metallocene for appropriate di-anionic ligands as the transition series is transcended from left to right (Scheme 1a) offers a systematic approach to the development of new molecular systems with the potential for "metallocene-like" reactivity. This relationship derives from the similar $1\sigma,2\pi$ bonding characteristics of certain mono- and di-anionic ligands which give rise to [CpML] and [ML_2] fragments with closely related frontier orbital characteristics: the basis of this 'isolobal' relationship has been outlined elsewhere (3).

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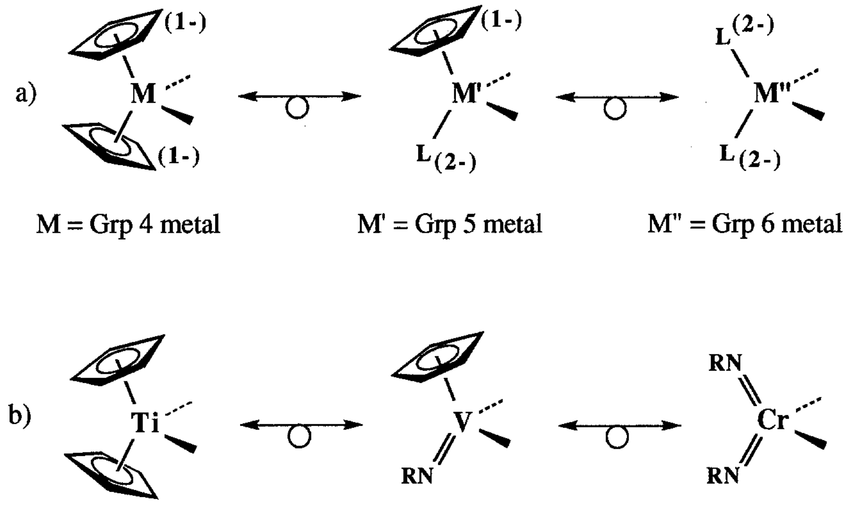

Scheme 1

Our approach has been to exchange Cp groups for organoimido (NR) ligands (3, 4), illustrated for the Ti→V→Cr series in Scheme 1(b). Here, we report on the ethylene polymerization activity of the Group 5 half-sandwich imido and Group 6 bis(imido) systems as conventional, dual-component catalysts derived from the transition metal dichlorides and Et_2AlCl (DEAC) or MAO as co-catalysts.

RESULTS AND DISCUSSION

The results of the polymerization runs, carried out under a flow of ethylene at 25°C in toluene solution, are collected in Table 1. Two points are worthy of note: first, the catalysts derived from the first row transition metal complexes $CpV(Ntol)Cl_2$ and $Cr(NBu^t)_2Cl_2$ are considerably more active than their second row counterparts, and secondly the vanadium-derived catalysts are more active than the chromium systems.

100 MHz ^{13}C NMR spectra recorded on polyethylene (PE) samples obtained from typical runs employing the vanadium and chromium catalysts showed that for both systems the resultant PE is of high molecular weight with little evidence of branching (< 1 per 5000 carbons). For the polymer derived from the vanadium catalyst, integration of the chain-end resonances versus the main-chain methylene carbons shows *ca.* 0.7 end-groups per 1000 carbons, compared with *ca.* 0.5 per 1000 carbons for the chromium derived sample; these correspond to number average molecular weights (M_n) of *ca.* 40,000 and 60,000 respectively. However, difficulties in completely solubilising the

samples indicate that these values underestimate the actual molecular weight of the polymer, a view supported by GPC analyses which reveal main peak M_w's of 2.1 x 10^5 and 1.2 x 10^6 respectively.

In summary, half-sandwich imido dihalide complexes of the Group 5 metals and bis(imido) dihalides of the Group 6 metals, in conjunction with DEAC or MAO as co-catalysts, are active catalysts for ethylene polymerization affording high molecular weight polyethylene with little branching.

Catalyst Precursor (mmol)	Activator (mmol/equiv.)	Yield Polyethylene (g)	Activity (gmmol^{-1}hr^{-1})
CpV(Ntol)Cl_2 (0.175)	Et_2AlCl (3.50/20)	0.44	15.1
CpV(Ntol)Cl_2 (0.007)	MAO (12/1715)	0.19	27.1
Cr(NBu^t)$_2$Cl$_2$ (0.193)	Et_2AlCl (3.86/20)	1.73	9.0
Cr(NBu^t)$_2$Cl$_2$ (0.040)	MAO (12/300)	0.19	4.4
CpNb(NAr)Cl_2 (0.120)	Et_2AlCl (3.60/30)	0.06	0.6
Mo(NBu^t)$_2$Cl$_2$ (0.160)	Et_2AlCl (3.20/20)	< 0.03	< 0.2

Table 1. Conditions: C_2H_4 (1 bar), 25°C, toluene solution. tol = tolyl; Ar = 2-Bu^{t}C$_6$H$_4$.

EXPERIMENTAL

GENERAL

CpV(Ntol)Cl_2 (5), Cr(NBu^t)$_2$Cl$_2$ (6), Mo(NBu^t)$_2$Cl$_2$ (7) were prepared by previously reported procedures. CpNb(N-2-Bu^{t}C$_6$H$_4$)Cl$_2$ was prepared by an analogous procedure to that described for CpNb(N-2,6-Pr$^i_2$C$_6$H$_3$)Cl$_2$ (3). Methylalumoxane (MAO) was prepared by the partial hydrolysis of trimethylaluminum using aluminum sulphate hydrate according to the procedure of Kaminsky (1). Et_2AlCl (1.8 M solution in toluene) was purchased from Aldrich Chemical Co. and used as received.

^{13}C NMR spectra were recorded in $C_2D_4Cl_2$/1,2,4-trichlorobenzene on a JEOL GX400 spectrometer operating at 100 MHz. GPC data were recorded on 0.02% w/v samples in trichlorobenzene solvent using a Waters 150 CV chromatograph fitted with Shodex 10^7 Å linear 10^4 Å columns, previously calibrated against polystyrene standards.

POLYMERIZATION RUNS

The polymerizations were carried out in a glass Schlenk vessel at 25°C in toluene solvent (75 mL). The ethylene gas was purified by passing through a column of $CaCl_2$, 4Å molecular sieves and P_2O_5, each separated by glass wool, followed by bubbling through a silicone oil bubbler (30 cm^3) to which 2 cm^3 of Et_2AlCl solution had been added. In a typical procedure, a toluene solution of Et_2AlCl was added *via* syringe to a stirred solution of the transition metal dihalide (0.05 g) in toluene (75 mL). The mixture was stirred for 10 min after which the solution was purged with a continuous stream of ethylene. After 1hr, the ethylene flow was stopped and the polymerization quenched by addition of a small amount of methanol. The resultant polymer was then isolated by filtration, washed sequentially with acidified methanol, methanol and toluene, and dried *in vacuo* overnight. For runs using MAO as co-catalyst, the MAO solution was first syringed into the reactor vessel followed by a toluene solution of the metal dihalide.

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