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Problems and solutions for alkene polymerisation catalysts incorporating Schiff-bases; migratory insertion and radical mechanisms of catalyst deactivation†

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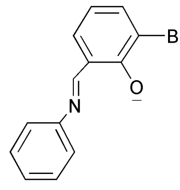
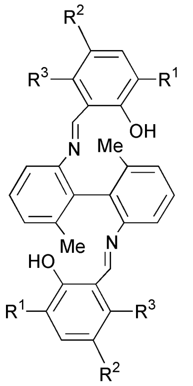
Steric blocking of an intramolecular 1,2-migratory insertion reaction of a zirconium salicylaldiminato complex leads to a long-lived catalyst for ethene polymerisation, but promotes a new radical catalyst decomposition mechanism in certain instances; kinetic and thermodynamic parameters for both pathways have been established.

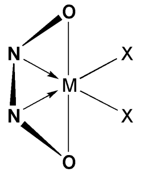
Complexes of the transition metals with imine ligands now have a central role in alkene polymerisation catalysis research.[1] In terms of catalyst activity and co-monomer tolerance, some of these systems, particularly those incorporating middle and later transition metals, compete with the metallocenes. Earlier metal catalysts such as the salicylaldiminato (*e.g.* **I**) complexes of titanium[2] and zirconium[3] display exceptionally high activity (> 4 × 10^6 kg mol^{-1} h^{-1} of PE for 5 min at 25 °C). The lifetime of these catalysts is however limited, particularly at the elevated temperatures used in industry. In this communication we report some preliminary investigations into the mechanisms by which group 4 Schiff-base catalysts may be deactivated, and describe a simple modification which converts an inactive catalyst into stable system.



I



R^1 = ^{t}Bu, R^2 = Me, R^3 = H **H_2L^1**
R^1 = ^{t}Bu, R^2 = H, R^3 = Me **H_2L^2**
R^1 = R^2 = Me, R^3 = H **H_2L^3**
R^1 = R^3 = Me, R^2 = H **H_2L^4**



α-*cis*-$[MLX_2]$

II

We have found that unlike SALEN-derived Schiff-base ligands, our chiral quadidentate biaryl-iminophenolate ligand system L gives, in its early and middle transition metal complexes, the α-*cis* **II**[4,5] or occasionally the β-*cis* structures.[5] The co-ligands X are forced to occupy mutually *cis* coordination sites; an important mechanistic criterion in many metal catalysed processes. Accordingly, such complexes have been successfully applied to enantioselective catalytic reactions in our laboratory.[6] Unfortunately however, despite the structural similarity[7] to Brintzinger's *ansa*-metallocenes,[8] our previous attempts to polymerise alkenes with $[MLX_2]$ (M = Ti, Zr; X = Cl, alkyls) under a variety of standard conditions has been unsuccessful; this can be traced to the fact that the imine unit(s) readily undergo intramolecular reduction, *i.e.* 1,2-migratory insertion (MI) with metal-bound alkyl ligands (Fig. 1).[5] Indeed, if the alkyls $[MLR_2]$ are susceptible to this type of reaction there is little hope that the more electrophilic alkyl cations $[MLR]^+$ of the type implicated in alkene polymerisation mechanisms will have significant lifetime under catalytic conditions.

Close examination of a previously published molecular structure $[ZrLCl_2]$[7] led us to the idea that the above 1,2-MI process could be slowed by placing an alkyl group at the position R^3 of the phenolate ring.‡ The type of substituted salicylaldehyde required has recently become available thanks to the work of Hofsløkken and Skattebøl.[9] The dramatic difference in stability between the catalyst $[ZrL^1Cl_2]$/MAO and that of the isomeric complex $[ZrL^2Cl_2]$ is detailed in Table 1 and Fig. 2; the rate of polymerisation is steady for at least 2 h at 25 °C. Similar results were obtained at 50 °C.†

To gain further insight into the stability of imine complexes of this type we undertook a kinetic study of alkyl complexes $[ZrL^n(CH_2Ph)_2]$ (n = 3, 4) which we found to decompose at rates that could be followed conveniently by ^{1}H NMR spectroscopy between 283 and 323 K. The orders of reaction were ascertained using suitable *n*th order plots and confirmed by Van't Hoff's method (ESI†). For complex $[ZrL^3(CH_2Ph)_2]$, which decomposed cleanly to a single product *via* 1,2-MI (Fig. 1),§ the expected first-order behaviour was observed. The subsequent Eyring plot gave an excellent fit leading to $\Delta H^‡$ = +87.7 ± 2.2 kJ mol^{-1} and $\Delta S^‡$ = −32 ± 8 J mol^{-1} K^{-1}. The latter figure indicates that a significant ordering of the system must occur in the path to the transition state of the migratory insertion reaction. This is consistent with our subsequent finding that the rate of the reaction is highly dependent on the steric demand of the substituent at the position R^1 (^{t}Bu > ^{i}Pr > Me);[10] the bulky groups force the metal bound alkyl group

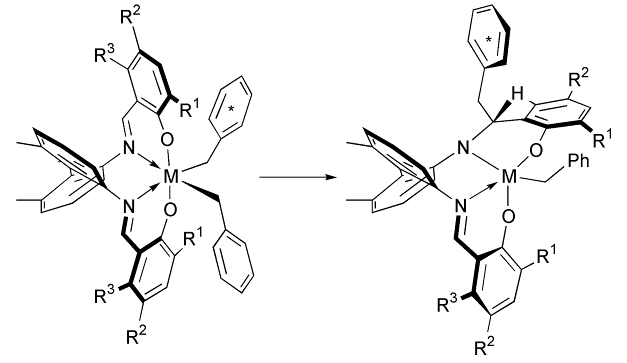


Fig. 1 1,2-Migratory insertion of alkyl at imine co-ligand in $[ML(CH_2Ph)_2]$ (M = Ti, Zr).

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† Electronic supplementary information (ESI) available: experimental details for the synthesis of all ligands and complexes, polymerisation data, further kinetic data along with treatment of errors, and a proposed radical propagation mechanism. See http://www.rsc.org/suppdata/cc/b1/b110423n/

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Table 1 Polymerisation of ethene using precatalysts [ZrLCl$_2$]

Entry	Complex	Cat./mmol	Cocatalyst	Temperature/°C	Yield/g	Activity/g PE (mmol-Zr bar-C$_2$ h)$^{-1}$
1^a	[ZrL^{1}Cl$_2$]	1.39×10^{-2}	MAO	25	0	—
2^a	[ZrL^{2}Cl$_2$]	1.39×10^{-2}	MAO	25	2.17	65
3^b	[ZrL^{1}Cl$_2$]	1.39×10^{-2}	MAO	50	0	—
4^b	[ZrL^{2}Cl$_2$]	1.39×10^{-2}	MAO	50	0.65	40

^{a} *Conditions*: solvent, toluene (150 ml); ethene pressure, 1.2 bar; polymerisation time, 2 h; Al:Zr molar ratio, 1000:1. ^{b} *Conditions*: solvent, toluene (500 ml); ethene pressure, 1.2 bar; polymerisation time, 1 h; Al:Zr molar ratio, 1000:1.

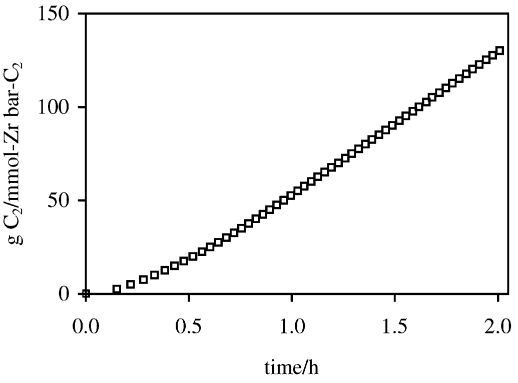

Fig. 2 Uptake of ethene with catalyst [ZrL^{2}Cl$_2$] (see Table 1).

toward the imine. The decomposition of the isomeric complex [ZrL^4(CH$_2$Ph)$_2$] gave a mixture of products, (ESI†) but nevertheless we have been able to unambiguously establish an order 1.5 for the reaction ($\Delta H^\ddagger = +100.7 \pm 4.8$ kJ mol^{-1} and $\Delta S^\ddagger = +16 \pm 16$ J mol^{-1} K^{-1}); these observations indicate a radical mechanism operating under Rice–Herzfeld (radical propagation) type kinetics.[11] We propose that this radical mechanism is made possible by the proximity of the (benzylic) R^3 methyl group to the imino C atom (Fig. 3) (ESI†). The 5-Me substituent thus provides a relatively low energy pathway for homolytic fission of the Zr–C bond. It is also important to note that the presence of a stable radical leaving group (*i.e.* benzyl) at the metal is also required for this process; the neopentyl complex [ZrL^4(CH$_2$Bu^t)$_2$] shows no significant decomposition products after days in solution.

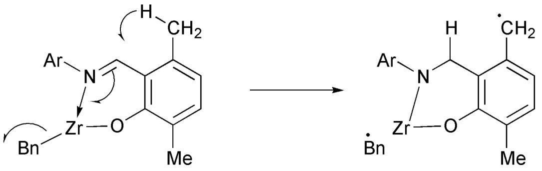

Fig. 3 Proposed initiation step in the radical decomposition of [ZrL^4(CH$_2$Ph)$_2$].

We have thus demonstrated a relatively simple ligand modification which sterically blocks a troublesome 1,2-MI reaction. This leads to a dramatic increase in the stability of the subsequent alkene polymerisation catalyst system, but only by virtue of the fact that the growing polymer chain R in the putative [ZrL^{4}R]$^+$ is not a good radical leaving group. We have begun to apply this modification to other catalytic problems, and have found that while [YL^1{N(SiMe$_2$H)$_2$}] is active for only 1-2 turnovers in intramolecular alkene hydroamination/cyclisation,[12] good conversion can be obtained using L^2. As another consequence of this work we might speculate that the susceptibility of aryliminophenolate ligands to radical damage, which we have previously observed in another context,[13] may be responsible for their unexpectedly poor performance in *e.g.* alkene epoxidation.[14]

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Notes and references

‡ Imine C-substitution (ref. 1) might have a similar effect but unfortunately the required salicylketimine proligands related to L$^{1-4}$ are not accessible.
§ This new complex eventually undergoes a second benzyl 1,2-MI reaction at the remaining imine unit.

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