Coordination Chemistry Reviews 255 (2011) 118–138

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Polymerization catalysis with transition metal amidinate and related complexes

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Contents

ARTICLE INFO

Article history:
Received 10 June 2010
Accepted 20 July 2010
Available online 27 July 2010

Keywords:
Metal
Amidinate
Polymerization
Olefin
Diene
Lactone

ABSTRACT

Applications of transition metal amidinate [$RC(NR')_2$], guanidinate and amidopyridine complexes to olefin coordination polymerization are reviewed. In addition, the use of complexes, featuring closely related ligands, such as phosphonamide or iminophosphonamide [$R_2P(NR')_2$], in olefin polymerization is highlighted. Some of these complexes have also been investigated in the stereoregular polymerization of styrene and conjugated dienes, whereas more recent work has focused on controlled ring-opening polymerization of lactones and lactides.

Abbreviations: MAO, methyaluminoxane; APy, amidopyridine; BR_3, $B(C_6F_5)_3$; $[Ph_3C][BR_4]$, $[Ph_3C][B(C_6F_5)_4]$; [DMAN][BR_4], $[PhNHMe_2][B(C_6F_5)_4]$; $[R_3NH][BR_4]$, $[R_2NHMe][B(C_6F_5)_4]$ with R_2 C_{16}–C_{18} di(hydrogenated tallow)amine; TIBAO, tetra-iso-butyl-di-aluminoxane; CGCTi, constrained geometry titanium complex; A, polymerization activity; MMAO, modified methyl aluminoxane; PMCP, poly(methylenecyclopentane); II, isotacticity index; β, stereoselectivity parameter; *m*, *meso* dyad; *mm*, *meso* triad, etc.; *r*, *racemic* dyad; α, $R_p/[R_p+R_{tr}]$ where the Schulz-Flory length distribution of oligomers is given by $f(n)$ $\alpha^n(1-\alpha)$; PNB, poly(norbornene); Hx^+, branches ≥6C atoms in length; ROP, ring-opening polymerization; PCL, poly(caprolactone); ε-CL, ε-caprolactone; LA, lactide; PLA, poly(lactic acid); PHB, poly(hydroxybutyrate); β-BL, β-butyrolactone; DIPP, 2,6-di-iso-propylphenyl; TIPP, 2,4,6-tri-isopropylphenyl.

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doi:10.1016/j.ccr.2010.07.005

1. Introduction

The area of metal amidinate and guanidinate chemistry has witnessed enormous growth over the past twenty years. The amidinate [$RC(NR')_2$] and guanidinate [$R_2NC(NR')_2^-$] ligands, which are considered sterically equivalent to η^5-cyclopentadienyl but, isoelectronic with π-allyl ligands, stabilize mononuclear main group, transition metal and lanthanide complexes, and can also serve as bridging ligands in di- or poly-nuclear metal complexes.

The coordination chemistry and synthesis of both transition metal and lanthanide amidinate and guanidinate complexes has been thoroughly reviewed recently by Edelmann in 2008–2009 and will not be discussed in detail here [1]. These reviews also included brief sections on the application of transition metal and lanthanide complexes towards olefin and polar monomer polymerization. A more extensive, though specialized, review of the synthesis and use of mono-, bis- and tris-(amidinate) complexes of group 4 in olefin polymerization appeared in 2007 [2]. However, this review neglected *inter alia* the important work of Sita and co-workers [3] as well as applications involving other transition metals.

The current review focuses in depth on the polymerization chemistry of transition metal amidinate and guanidinate catalysts and where possible, a detailed discussion of the mechanistic issues involved. In addition to [$RC(NR')_2$] complexes, there have also been reports on the use of isoelectronic complexes based on amidate [RC(=O)NR′] and thioamidate [RC(=S)NR′] ligands in polymerization catalysis. Finally, this review also summarizes our previous work [4] concerned with the study of P(V) analogs – i.e. iminophosphonamide [$R_2P(NR')_2$] complexes [5] as well as recent work on the related (thio)phosphonamide complexes [$R_2P(=S)NR'$; $R_2P(=O)NR'$].

The use of transition metal [$RC(NR')_2$] complexes in polymerization catalysis can be divided into two principle areas, one involving the coordination polymerization of simple olefins and non-conjugated α,ω-dienes, and the other involving polar monomer polymerization, including styrene and conjugated dienes. There are often strong analogies between the latter processes, and anionic addition or ring-opening polymerization involving main group metal alkyls or related initiators. Especially, lanthanide complexes have featured prominently in the latter area where the polar and ionic character of lanthanide metal bonds suggests strong analogies to some main group initiators. We discuss these two areas separately in the current review since they can be mechanistically quite distinct from the chemistry involved in coordination polymerization. It should be mentioned that [$RC(NR')_2$] complexes have also been employed in the dehydrogenative coupling of silanes to form polysilanes [6], and in atom transfer radical polymerization (ATRP, *vide infra*). In fact, it is debatable in isolated cases whether some polymerizations observed using transition metal [$RC(NR')_2$] complexes are properly described as coordination polymerization vs. other processes.

1.1. Olefin coordination polymerization using transition metal amidinate complexes

Ethylene and in some cases, higher α-olefins, have been polymerized using [$RC(NR')_2$] or related complexes of just about every 1st row element of the transition metals. However, it should be borne in mind that some of these citations arise from the patent literature and it is debatable in those cases whether all compositions claimed were tested.

From a historical perspective, the first literature report on the use of a transition metal amidinate complex in ethylene polymerization dates back to the work of Green and co-workers, who reported in 1993 that the complex $Cp[PhC(NTMS)_2]ZrCl_2$ was active in ethylene and propene polymerization upon activation with methylaluminoxane [7]. The first patent application on the use of an amidinate complex in olefin polymerization concerns the work of Idemitsu, where in 1994 the complex $[PhC(NTMS)_2]_2ZrCl_2$ was activated for ethylene polymerization using Al^iBu_3 and $[PhNHMe_2][B(C_6F_5)_4]$ [8]. The first patent to actually issue in this area (in 1998 as US Patent 5,707,913 [9]) concerns related work reported by BASF AG in 1995 where the same complex was activated by methylaluminoxane (MAO) for ethylene polymerization [10]. Other early patent applications include that on the use of Ti mono-amidinate complexes for styrene polymerization, forming syndiotactic polystyrene [11], and that of Borealis covering the use of 2-amidopyridine (APy) complexes of groups 4–6 in ethylene polymerization upon activation with MAO [12].

However, if we include isoelectronic or isostructural ligands, the first report on the use of a transition metal [$R_2P(NR')_2$] complex in ethylene polymerization dates back to the work of Keim and co-workers in 1981 (!) where a π-allylnickel [$R_2P(NR')_2$] complex was thought to be active in ethylene polymerization [13]. While subsequent work revealed that these discrete complexes are actually inactive for ethylene polymerization [4], nevertheless the species formed *in situ* from $Ni(\eta^3\text{-}C_3H_5)_2$ and $(Me_3Si)_2NP(=NSiMe_3)_2$, *in the presence of ethylene*, is undoubtedly an $[R_2P(NR')_2]NiR(L)$ complex (*vide infra*).

1.1.1. Ethylene polymerization using group 4 amidinate complexes

Of the transition elements, it is correct to conclude that the vast majority of published work in olefin polymerization has dealt with complexes of group 4. The classes of complexes that have been studied in ethylene polymerization are summarized in Chart 1 and representative results are listed in Table 1 along with relevant literature citations. The complexes listed in Chart 1 are in roughly chronological order of their use for ethylene polymerization. In Table 1, most of the complexes listed were activated with MAO , unless otherwise noted, while selected studies dealing with alkyls and discrete activators will be discussed subsequently.

In reviewing the results in Table 1 it can be seen that activities in ethylene polymerization, upon activation with MAO, vary by more than four orders of magnitude for complexes of the *same*

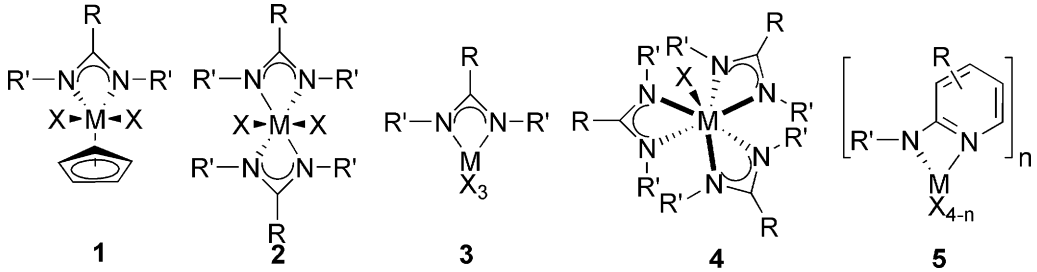


Chart 1.

Table 1
Amidinate complexes of group 4 in ethylene polymerization.

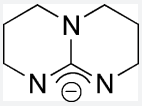
Entry	M	R	R′[a]	X	Cp	Conditions[b]	Activity[c]	M_w (kg mol^{-1})	PDI[d]	Ref.
Cyclopentadienyl(amidinate) complexes ***1***										
1	Zr	Ph	$SiMe_3$	Cl	C_5H_5	840:1, 2 bar, 25 °C	6.15×10^4	–	–	[7]
2	Zr	Ph	$SiMe_3$	Cl	C_5H_5	4000:1, 5 bar, 80 °C	1.90×10^6	111	2.8	[18]
3	Ti	Me	Cy	Me	C_5H_5	25 °C	2.2×10^4	–	–	[19]
4	Ti	Me	^{t}Bu, 2,6-Me_2Ph	Me	C_5H_5	25 °C	1.0×10^2	–	–	[19]
5	Ti	Me	various	Me	C_5Me_5	25 °C	Inactive			[19]
Bis(amidinate) complexes ***2***										
6	Zr	Ph or p-Tol	$SiMe_3$	Cl		200–800:1, 1–5 bar, 5–60 °C	6.50×10^3-5.70×10^5	M_η = 30–160	–	[20]
7	Zr	Ph	$SiMe_3$	Cl		2000:1, 0.69 bar, 20 °C	1.86×10^4	–	–	[21]
8	Zr	Ph	$SiMe_3$	Cl		100:1, 1 bar, 30 °C	ca. 10^3	–	–	[14]
9	Ti	Ph	$SiMe_3$	Cl		2000:1, 0.69 bar, 20 °C	6.96×10^3	–	–	[21]
10	Ti	Ph	$SiMe_3$	Cl		1000:1, 20 bar, 20 °C	5.80×10^3	–	–	[17]
11	Ti	Me	Cy	Cl		360:1, 1 bar, 20 °C	7.00×10^3	503	40	[22]
12	Zr	Me	Cy	Cl		100–1300:1, 1 bar, 20 °C	$\leq 1.6 \times 10^4$	700–790	38–87	[22]
13	Zr	Me	Cy	Me		1240:1, 1 bar, 20 °C	–	449	31	[22]
14	Zr	tBu	Cy	Cl		100–1250:1, 1 bar, 20 °C	–	865	20	[22]
15	Hf	Me	Cy	Cl		380:1, 1 bar, 20 °C	–	755	15	[22]
16	Ti	Ph	^{i}Pr	Cl		200:1, 1 bar, 25 °C	1.20×10^5	–	–	[23]
17	Zr	Ph	^{i}Pr	Cl		200–2000:1, 1 bar, 25 °C	0.68–6.0×10^4	–	–	[23]
18	Zr	Ph	^{i}Pr	Cl		400–2000:1, 1 bar, 60 °C	0.86–4.0×10^5	–	–	[23]
19	Zr	NMe_2	^{i}Pr	Cl		500:1, 7.3 bar, 75 °C	3.20×10^5	–	24.8	[24]
20	Ti	hpp= 		Cl		1000:1, 7.5 bar, 25 °C	2.20–7.40×10^3	–	–	[25]
21	Zr	Ph	2,6-iPr_2Ph	Me		[DMAN][BR_4][e], 5 bar, 50 °C	Inactive	–	–	[26]
22	Zr	Ph	2,6-iPr_2Ph, 2,6-Me_2Ph	Me		[DMAN][BR_4][e], 5 bar, 50 °C	1.42–1.94×10^2	10–60	Bimodal	[26]
23	Zr	p-Tol	Ph, $SiMe_3$	Cl		500:1, 1 bar, 25 °C	7.7×10^3	–	–	[15]
Mono(amidinate) complexes ***3***										
24	Ti	p-Tol	Me	Cl		2000–4000:1, 1 bar, 20 °C	2.13–3.07×10^4	78-103	–	[21]
25	Ti	Ph	$SiMe_3$	Cl		2000:1, 0.69 bar, 20 °C	2.44×10^4	–	–	[21]
26	Ti	Ph	$SiMe_3$	Cl		1000:1, 20 bar, 20 °C	5.60×10^3	–	–	[17]
27	Ti(III)	Ph	$SiMe_3$	Cl		$MgCl_2$/AlR_3, 1 bar, 50 °C	2.25×10^7	602	2.3	[27]
28	Ti	Ph	$SiMe_3$	O^{i}Pr		2000:1, 0.69 bar, 20 °C	7.54×10^3	–	–	[21]
29	Zr	Ph	$SiMe_3$	Cl		100:1, 1 bar, 30 °C	ca. 10^3	–	–	[14]
30	Ti	[f]	Ph, ^{t}Bu	NMe_2		1200:1, 2 bar, 25 °C	1.7–11.2×10^4	–	–	[28]
31	Zr	[f]	Ph, ^{t}Bu	NMe_2		1200:1, 2 bar, 25 °C	0.7–9.7×10^3	–	–	[28]
32	Zr	[g]	Ph, ^{t}Bu	NMe_2		2400:1, 2 bar, 25 °C	4.1–13.7×10^3	–	–	[28]
33	Zr	NMe_2	$SiMe_3$, 2,6-^{i}Pr_2Ph	Cl		1000–4000:1, 10 bar, 20–80 °C	2.15–6.48×10^4	M_w = 723–95.0	13–2.5	[29]
Tris(amidinate) complexes ***4***										
34	Zr	Ph	$SiMe_3$	Cl		100:1, 1 bar, 30 °C	ca. 10^3	–	–	[14]
35	Zr	p-Tol	Ph, $SiMe_3$	Cl		500:1, 1 bar, 25 °C	8.6×10^3	–	–	[15]
36	Zr	NMe_2	Ph, $SiMe_3$	Cl		1000:1, 10 bar, 25 °C	1.04×10^4	M_n = 18	–	[16]
37	Zr	1-Piperidyl	Ph, $SiMe_3$	Cl		1000:1, 10 bar, 25 °C	1.50×10^4	–	–	[16]
38	Hf	NMe_2	Ph, $SiMe_3$	Cl		500–2000:1, 10 bar, 20–80 °C	Trace-2.74×10^4	M_n = 11–350	–	[16]
39	Hf	1-Piperidyl	Ph, $SiMe_3$	Cl		1000:1, 10 bar, 25 °C	9.36×10^2	M_n = 3.50	–	[16]
Amidopyridine complexes ***5***										
40	Zr	H	Ad	Cl	2	1 bar, 25 °C	2.0×10^4	–	–	[30]
41	Ti	6-Me	[h]	Cl	2	1 bar, 25 °C	1.8×10^4	–	–	[31]
42	Ti	H	Ph	Cl	1	3000:1, 3–5 bar, 60–80 °C	2.17–3.78×10^4	135–804	2.5–4.2	[32]
43	Ti(III)	H	Ph	Cl	1	3000:1, 5 bar, 60 °C	5.70×10^4	799	3.0	[32]
44	Ti	H	Ph	Cl	2	3000:1, 5 bar, 60 °C	1.90×10^4	239	2.4	[32]
45	Zr	6-[2,6-Me_2Ph]	2,6-^{i}Pr_2Ph	Cl	2	500:1, 5 bar, 50–80 °C	2.80–3.28×10^5	675–790	14.6–35.3	[33]
46	Zr	6-[2,6-Me_2Ph]	2,6-^{i}Pr_2Ph	Me	2	TIBAO 50:1, [R_3NH][BR_4][i], 5 bar, 30–100 °C	7.60–44.4×10^5	12.1–9.0	~2	[33]
47	Zr	6-[2,4,6-iPr_3Ph]	2,6-^{i}Pr_2Ph	Cl	2	500:1, 5 bar, 30–100 °C	1.60–27.6×10^5	891–392	15.1–2.2	[33]
48	Zr	6-[2,4,6-iPr_3Ph]	2,6-^{i}Pr_2Ph	Me	2	TIBAO 50:1, [R_3NH][BR_4][i], 5 bar, 30–100 °C	1.40–3.76×10^6	1830–1010	Multimodal	[33]
49	Ti	H	Ph	Cl	2	3000:1, 5 bar, 60 °C	1.60×10^4	250	2.5	[34]
50	Ti	H	2-EtPh	Cl	2	3000:1, 5 bar, 60 °C	5.40×10^3	630	Bimodal	[34]
51	Ti	H	3,5-Me_2Ph	Cl	2	3000:1, 5 bar, 60 °C	9.40×10^3	390	Bimodal	[34]
52	Ti	H	4-^{n}BuPh	Cl	2	3000:1, 5 bar, 60 °C	9.60×10^3	500	Bimodal	[34]
53	Ti	H	2-^{t}BuPh	Cl	2	3000:1, 5 bar, 60 °C	6.00×10^3	390	Bimodal	[34]
54	Ti	H	2,6-F_2Ph	Cl	2	3000:1, 5 bar, 60 °C	1.34×10^4	604	4.5	[35]
55	Ti	H	Ph	Cl	2	3000:1, 5 bar, 60 °C	1.90×10^4	239	2.4	[35]
56	Ti	H	2-ClPh	Cl	2	3000:1, 5 bar, 60 °C	1.12×10^4	344	12.4	[36]

Table 1 (*Continued*)

Entry	M	R	R′[a]	X	*n*	Conditions[b]	Activity[c]	M_w (kg mol^{-1})	PDI[d]	Ref
57	Ti	H	2,6-F_2Ph	Cl	1	3000:1, 3–8 bar, 60–80 °C	$2.03–8.00 \times 10^4$	309–1392	2.1–6.9	[35]
58	Zr	6-[2,4,6-iPr_3Ph]	2,6-^{i}Pr_2Ph	Bn	1	TIBAL 55:1, BR_3 2.2:1, 5 bar, 80 °C	1.20×10^5	1130	1.90	[36]
59	Zr	6-[2,4,6-iPr_3Ph]	2,6-^{i}Pr_2Ph	Bn	1	TIBAO 50:1, [R_3NH][BR_4][i] 2.2:1, 5 bar, 80 °C	1.12×10^6	71.8	21.6	[36]
60	Hf	6-[2,4,6-iPr_3Ph]	2,6-^{i}Pr_2Ph	Bn	1	TIBAL 55:1, [R_3NH][BR_4][i] 2.2:1, 5 bar, 80 °C	1.20×10^6	108	3.1	[36]
61	Zr	6-[2,6-Me_2Ph]	2,6-^{i}Pr_2Ph	Bn	1	TIBAO 50:1, [R_3NH][BR_4][i] 2.2:1, 5 bar, 50 °C	6.4×10^5	328	62.3	[36]
62	Zr	6-[2,4,6-iPr_3Ph]	2,6-Me_2Ph	Bn	1	TIBAO 50:1, [R_3NH][BR_4][i] 2.2:1, 5 bar, 50 °C	4.8×10^5	45.2	14.2	[36]

[a] If two groups are separated by a comma, the ligand is unsymmetrical.
[b] Al:Zr ratio, *P*, *T* where Al:Zr ratio is for MAO unless otherwise stated.
[c] Activity is in g PE mol M^{-1} bar^{-1} h^{-1}.
[d] PDI = polydispersity index = M_w/M_n.
[e] [DMAN][BR_4] = [$PhNHMe_2$][$B(C_6F_5)_4$].
[f] R = –C(N^{t}Bu)(NPh)M(NMe_2)$_3$.
[g] R = –C(=N^{t}Bu)NHPh.
[h] 2,2′-[(6-Me)C_6H_3-(6′-Me)C_6H_3].
[i] [R_3NH][BR_4] = [R_2NHMe][$B(C_6F_5)_4$] with R_2 = C_{16}–C_{18} di(hydrogenated tallow)amine.

class. This variation is unusual in comparison with the performance of e.g. metallocene complexes of group 4 (even amongst different research groups) and suggests inefficient activation and/or poor catalyst stability under the conditions studied. Inefficient activation is suggested, as in some cases, dramatically improved activities were observed at higher *T* using the same catalyst. The other thing to note, at least in cases where such data are reported, is that many of the complexes studied do not furnish PE with a unimodal molecular weight distribution with PDI = polydispersity index = $M_w/M_n \sim 2$. This finding is also consistent with poor catalyst stability (i.e. multi-site behavior), though some authors have also attributed this feature to poor heat and/or mass transfer during polymerization.

That heat and/or mass transfer effects are of importance is undisputed, and the variations seen, when comparing the results of different research groups using the *same* complex, sometimes reflect this. For example, in comparing entries 1 and 2 of Table 1, the 100-fold increase in activity observed can be almost entirely attributed to the difference in *T* of polymerization, coupled with the lower solubility of ethylene in solution at the higher *T* (i.e. despite the use of higher *P*). On the other hand, the difference in activity seen in entries 9 vs. 10 or 25 vs. 26, where use of significantly higher *P* and marginally lower Al:M ratios, result in somewhat *lower* activity at the *same T*, must result from mass transfer limited conditions and/or purity problems.

Some authors also attribute polymer insolubility in the reaction medium as a cause for broad MWD. If the reactor is very inefficiently stirred and/or cooled they have a point! However, assuming proper *T* control and effective agitation, a single site catalyst will produce an insoluble polymer with a PDI ≤ 3.0 if the catalyst is otherwise stable and the polymer is not branched, through e.g. macro-monomer incorporation. A broad or even bimodal MWD could also be encountered if there were a process, usually second order in living and dormant chains, that otherwise leads to a narrowing of the MWD in solution, such as (reversible) chain transfer to Al or a related process.

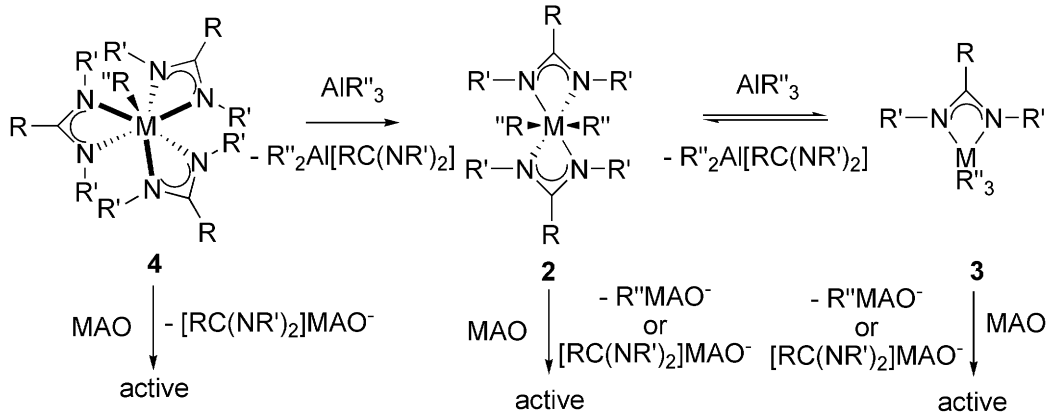
In comparing different metals with the same ligands, no clear trends emerge. For example, entries 7 and 9 show that the Zr complex is about 3× more active than its Ti analog, while the opposite trend is seen in entries 16 and 17. Similar ambiguity pertains to the case of Zr vs. Hf, where more often than not, essentially similar activities (and in some cases MW) are observed. In the case of Ti, it is safe to say that the oxidation state of the metal is important, though the comparison involves soluble Ti(IV) vs. a supported Ti(III) catalyst (entries 24–26 vs. 27). A more direct comparison is seen in entries 42 and 43, where it seems probable that under *both* conditions, the most active species present is a Ti(III)–monoamidinate complex. MAO is known to effect *in situ* reduction of Ti in other catalyst systems so this result is not that surprising.

Steric effects are obviously important with these complexes; for example in mixed Cp[$RC(NR'')_2$]Ti complexes, only the less hindered Cp complexes were active (entries 3–5) and similar behavior was encountered in sterically hindered bis-[$RC(NR'')_2$] complexes (entry 21 vs. 22). In this specific case, the structure of the ion-pair (*vide infra*) accounted for this difference. The opposite kind of behavior is seen in sterically hindered, APy Zr complexes (entries 45 vs. 47) though this appears to be activator dependent (see entries 46 vs. 47 and also entries 58–59 vs. 61 and 62) and was attributed to inefficient activation vs. competing ligand abstraction by MAO in this particular case.

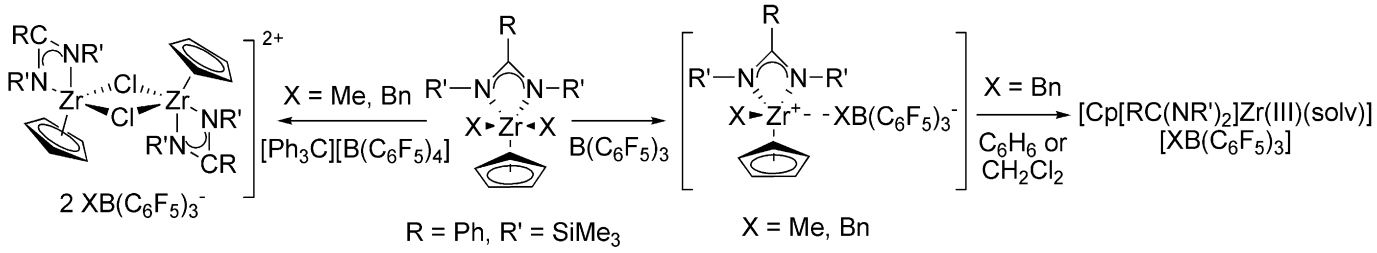
A limited number of guanidinate complexes of group 4 have been tested and where comparisons are possible, the activity of these catalysts does not differ greatly from their [$RC(NR'')_2$] analogs (see entries 17–19 and also 34–37). This is surprising as guanidinate ligands are significantly more electron rich than [$RC(NR'')_2$] ligands. On the other hand, to judge from the results reported in entries 54–56, electronic effects mainly manifest themselves in changes to MW rather than activity, though a systematic study involving isosteric catalysts has not yet been reported.

Finally, it should be noted that tris(amidinate) complexes **4** should be inactive, if activation by MAO involves alkylation and alkide abstraction. The fact that such complexes are active strongly indicates either [$RC(NR'')_2$] ligand abstraction, or at least modification, by MAO (or by $AlMe_3$ which is a component of MAO) is involved (e.g. Scheme 1) [14–16]. In fact, it seems quite probable that similar processes may intervene in the case of unhindered bis- vs. mono-[$RC(NR'')_2$] complexes as their activity differences are often negligible [17]. This complexity should have been evident from the MWD of the PE formed – i.e. assuming each species is reactive towards polymerization but with different k_p/k_{tr} characteristics. Unfortunately this was not evaluated in much of the early work in this area. In more recent work, one cause of the bi- or multi-modality seen may involve such reactions. However, some reactions that produce bi- or multi-modal PE do not involve MAO-activation; in these cases, alkylaluminum compounds were employed as scavenging agents, and these, or more reactive species like [AlR''_2][$B(C_6F_5)_4$] formed *in situ*, may have engaged in similar reactions.

Early work from the group of Green and co-workers illustrated the complexity of activation, especially when compared to metallocene complexes [37]. Reaction of Cp[$RC(NR'')_2$]$ZrMe_2$ or Cp[$RC(NR'')_2$]$ZrBn_2$ with $B(C_6F_5)_3$ (BR_3) afforded the expected ion-pairs in solution; however, that derived from the benzyl complex was unstable with respect to reduction to Zr(III)! Reaction of Cp[$RC(NR'')_2$]$ZrMe_2$, Cp[$RC(NR'')_2$]$ZrBn_2$ or Cp*[$RC(NR'')_2$]$ZrMe_2$ with [Ph_3C][$B(C_6F_5)_4$] ([Ph_3C][BR_4]) in CH_2Cl_2 solution did not afford the expected ion-pairs. Instead, stable dicationic prod-



Scheme 1.



Scheme 2.

ucts resulting from halogen abstraction/anion degradation were obtained (Scheme 2).

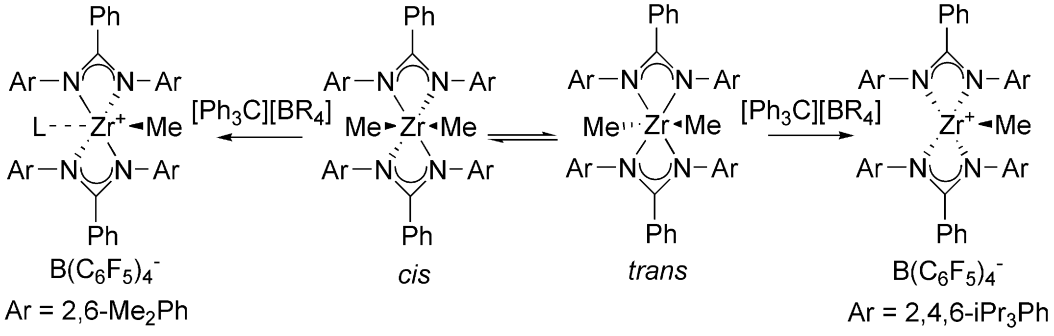
It is difficult to reconcile these early results with the much cleaner chemistry exhibited by the Cp $[RC(NR'')_2]$ complexes studied by Sita and co-workers (*vide infra*) [3] or more electron rich guanidinate [24] and $Cp[R_2P(NR'')_2]$ complexes [4] studied by others, where the expected ion-pairs are indefinitely stable in a variety of solvents. On the other hand, all of these complexes appear prone to, e.g. C–H activation and so changes to any of the ligands often lead to unexpected consequences upon ionization.

The work of Hessen, Kempe and co-workers on the synthesis of very hindered bis-$[RC(NR'')_2]$ [26] or bis- [33] or mono-APy complexes [36] has been quite instructive; with sufficiently bulky substituents, the bis-$[RC(NR'')_2]$ dihalides or dialkyls can adopt distorted *trans* vs. *cis* octahedral geometries (Scheme 3), while an ion-pair derived from the most hindered dialkyl $[RC(NR'')_2]$ complex adopted a distorted, square pyramidal geometry with the alkyl group occupying the apical position. This complex was found to be unreactive towards ethylene since there was no available *cis* coordination site, while less hindered complexes, particularly those derived from APy ligands, afforded more active catalysts due to their ability to adopt the expected *cis*-octahedral geometry.

The picture that emerges from these studies is that $[RC(NR'')_2]$ complexes or their variants are significantly less active in ethylene polymerization than metallocene complexes as a consequence of inefficient activation by MAO, poor catalyst stability towards AlR_3 and/or extreme steric hindrance at the metal center, in addition to any intrinsic differences. On the other hand, more recent work on both $[RC(NR'')_2]$ and APy complexes suggest that the activity differences might not be as pronounced as originally thought, especially when these complexes are activated under optimal conditions (e.g. $A \sim 10^6$ kg PE mol M^{-1} h^{-1} bar^{-1} vs. 10^7–10^8 kg PE mol M^{-1} h^{-1} bar^{-1}). In fact, in one case (Table 1, entry 2), the activity of the $Cp[RC(NR'')_2]ZrCl_2$ complex studied and Cp_2ZrCl_2 were essentially identical [18]!

1.1.2. Ethylene polymerization using group 4 pyridinethiolate and amidate complexes

A few studies report the activation of amidate [RC(=O)NR'] or pyridine-2-thiolate complexes of group 4 for ethylene polymerization using MAO. Erker and co-workers reported the preparation of constrained geometry $CH_2{=}C(C_5Me_4)[\kappa^2\text{-}NC(=O)R]ZrCl_2$ complexes in a patent application and subsequent paper [38]. However, none of these complexes were activated for ethylene polymerization, though their use in that process is claimed.



Scheme 3.

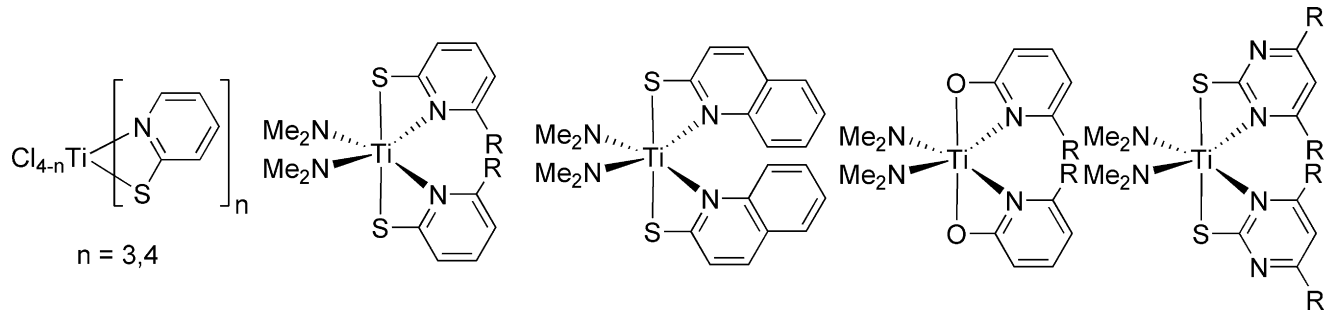
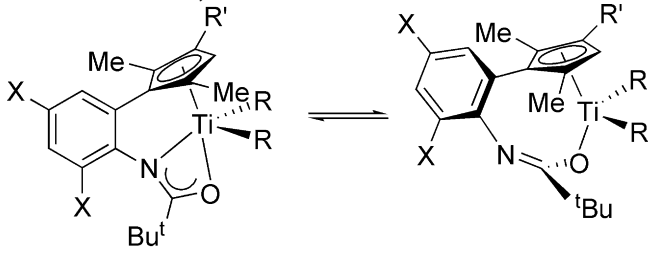


Chart 2.

A number of pyridine-2-thiolate, quinoline-2-thiolate, 6-R-2-pyridone, [39] and 4,6-R_2-pyrimidine-2-thiolate complexes of Ti(IV) and Zr(IV) were prepared and evaluated for ethylene (and styrene) polymerization, upon activation with excess MAO (Chart 2) [40]. Bis-, tris-, tetrakis-pyridine-2-thiolate and bis-quinoline-2-thiolate Ti complexes exhibited productivities of 0.56–2.3 kg PE mol Ti^{-1} h^{-1} bar^{-1} upon activation with MAO or modified MAO (MMAO) at room temperature. Though the catalysts showed higher activity at sub-ambient *T*, the PE formed in all cases exhibited extremely broad MWD (with PDI = 5.7–192!). Vastly improved activities were observed for (6-R-pyridine-2-thiolate)$_2$Ti(NMe_2)$_2$ complexes, with *A* = 53, 980, 1100 and 1200 kg PE mol Ti^{-1} h^{-1} bar^{-1} for R = Me, Ph, p-tolyl, and m-xylyl, respectively at 60 °C. Again, the PE formed had a broad MWD with PDI = 11–96. Zirconium analogues of the m-xylyl complexes were much less active, as were 6-Ph-2-pyridone complexes of Ti. Finally, an electron deficient (4,6-R_2-pyrimidine-2-thiolate)$_2$Ti(NMe_2)$_2$ complex (R = CF_3) was about 10× more active than the non-fluorinated analog (R = Me, *A* = 2.2 kg mol Ti^{-1} h bar^{-1} at 60 °C), but again both provided PE with a broad and multi-modal MWD. Evidently, ligand abstraction in the presence of MAO gave rise to multiple active species under all conditions examined.

A limited number of o-phenylene bridged, Cp(amidato) complexes of Ti were prepared by Joung et al. *via* amine elimination reactions [41]. In some cases, the amidato ligand was cleaved from the metal on work-up with silyl halides and transformed into a dangling, α-chloroimine group. Of the amidato products isolated, isomerization between κ^1-O and κ^2-N,O forms occurred in solution (X = F). Activation with TIBAL and $[Ph_3C][BR_4]$ for ethylene-1-octene copolymerization at 90 °C and 13 bar afforded low density copolymers containing 20–30 mol% 1-octene at productivities of 1.54–5.15 × 10^6 g POE mol Ti^{-1} h^{-1} bar^{-1}, only slightly less active than a CGCTi catalyst under the same conditions, and which featured similar levels of 1-octene incorporation. Moreover, the MW of the copolymers formed using the Cp[RC(=O)NR′] complexes were 2–4 times higher (M_w = 100–200 K), though with a broader MWD (PDI = 4.6–6.9 vs. 2.8).



1.1.3. Ethylene polymerization using group 4 iminophosphonamide complexes

Collins and co-workers reported the first examples of ethylene polymerization using bis-[$R_2P(NR')_2$] and Cp[$R_2P(NR')_2$] complexes of group 4 [4i]; these complexes are readily available through amine or alkane elimination reactions [4f]. Under the conditions studied (50–70 °C, 5 bar) many compositions exhibited single-site behavior upon activation with MAO (M_n = 79–213 K, with PDI = 1.7–3.6) with productivities ($A = 0.40–1.74 \times 10^6$ g PE mol Zr^{-1} h^{-1} bar^{-1}) that exceeded those of [$RC(NR')_2$] catalysts examined under similar conditions (*cf.* Table 1). The Ti complexes were about 22–140× less active than their Zr counterparts and afforded lower MW polymer. A limited number of $R_2P(NR')$=O complexes were also prepared in a companion patent application [4h]; these too were active for ethylene polymerization upon activation with MAO, though they were generally 1–2 orders of magnitude less active than their [$R_2P(NR')_2$] analogues.

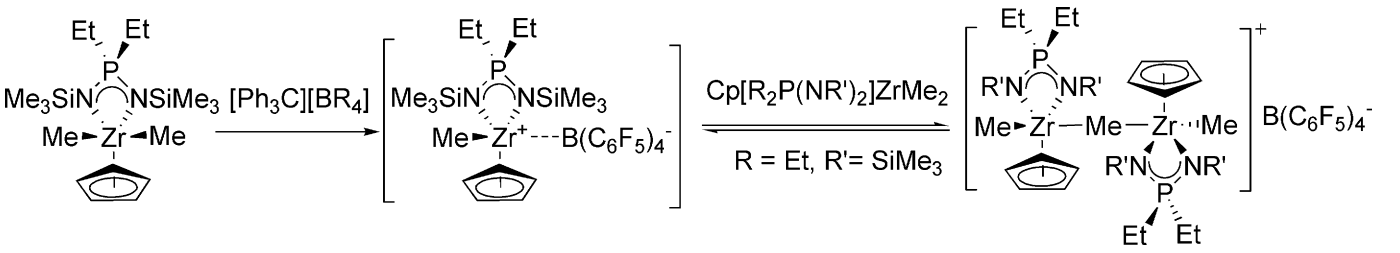
Subsequent work focused on the Cp[$R_2P(NR')_2$]Zr complexes, as these were the most active of those originally screened. However, at much higher *T* in a solution process, multi-site behavior was observed upon activation with MAO [4h]. Detailed study of these complexes in ethylene polymerization at lower *T* in toluene suspension revealed that many examples of these Cp[$R_2P(NR')_2$] complexes also showed complicated behavior on activation with MAO, forming PE with a bimodal MWD [4d].

This was eventually traced to $AlMe_3$-mediated ligand abstraction; when the dimethyl complexes were activated with $[Ph_3C][BR_4]$, optimally in the presence of small quantities of MAO, or mixtures of excess $MeAl(BHT)_2$ and $AlMe_3$ as scavenging agents [42], single site behavior was observed. Activities were nearly double under these conditions ($A = 3.69 \times 10^6$ g PE mol Zr^{-1} h^{-1} bar^{-1}) with formation of high MW PE (M_n 150 K with PDI = 1.90).

^{31}P (and ^{1}H) NMR spectroscopic monitoring of a mixture of Cp[$R_2P(NR')_2$]$ZrMe_2$ and MAO (50:1 Al:Zr) revealed formation of a $Me_2Al[R_2P(NR')_2]$ complex, as well as the expected ion-pair, by comparison to that formed from $[Ph_3C][BR_4]$. As with metallocenium ions [43], the ^{31}P (and ^{1}H) NMR signals of the ion-pair were line-broadened[1] at these low Al:Zr ratios due to different species being present. Evidently, some of the PE formed in the presence of excess MAO was generated from either an unstable [$CpZrMe_2$][MAO] catalyst or a more stable [Cp_2ZrMe][MAO] catalyst, formed by disproportionation of $CpZrMe_3$, and subsequent activation of Cp_2ZrMe_2.

Solution NMR studies of the ion-pairs formed from the Cp[$R_2P(NR')_2$]$ZrMe_2$ complexes and $[Ph_3C][BR_4]$ revealed that these were indefinitely stable in haloarene solution at ambient *T* or even CH_2Cl_2 solution at lower *T*. Like their Cp[$RC(NR')_2$] analogues (*vide infra*), they also form μ-Me adducts with excess Cp[$R_2P(NR')_2$]$ZrMe_2$ that are fluxional on the NMR time scale. There are two processes involved, reversible dissociation into the two components, and Me, μ-Me ligand exchange within the dinuclear complex. The latter process has the lower activation energy and interconverts *rac* and *meso* stereoisomers.

[1] We have no evidence for Al-mediated reduction of Zr in our work, as reported by Eisen and coworkers (*vide infra*), though admittedly we did not examine our solutions by ESR spectroscopy. NMR signals due to other diamagnetic compounds present were not noticeably line-broadened in these experiments.



These stable ion-pairs were briefly evaluated for living 1-hexene polymerization under conditions reported by Sita and co-workers (*vide infra*). They were less active and based upon initiator efficiencies, exhibited significant chain transfer at 25 °C compared to [Cp{MeC(N^{t}Bu)(NEt)}ZrMe][$B(C_6F_5)_4$].

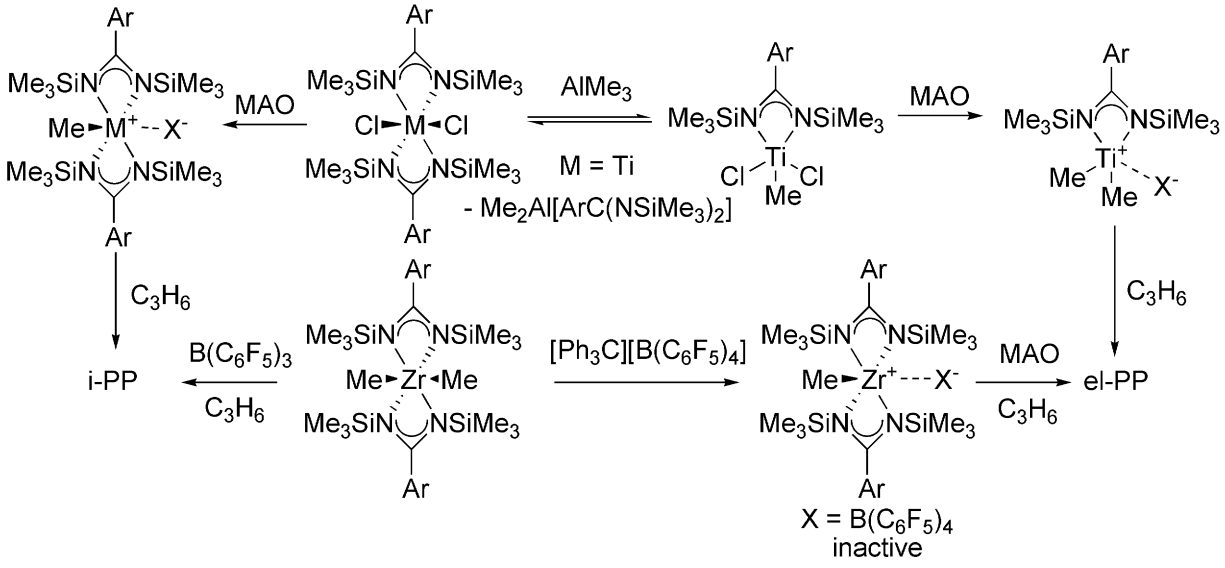
It should be mentioned that an independent study showed that more hindered $[Ph_2P(NR)(N^tBu)]_2MCl_2$ (R = Ph, $SiMe_3$, M = Ti, Zr) complexes were *inactive* for ethylene polymerization using either excess MMAO or TIBAL/[Ph_3C][BR_4] at room temperature and 1 bar [44]. We also noted significant decreases in activity at lower *T* and *P* in our earlier work with some catalysts [4i–h]. It is possible, in view of the results obtained for the Cp[$R_2P(NR'_2)$] complexes, that MAO-mediated ligand abstraction from the bis-[$R_2P(NR'_2)$] complexes to furnish mono-[$R_2P(NR'_2)$] catalysts is only effective at higher *T* and that these are the actual active species; follow up studies have not been reported.

1.1.4. Propylene polymerization using group 4 amidinate complexes

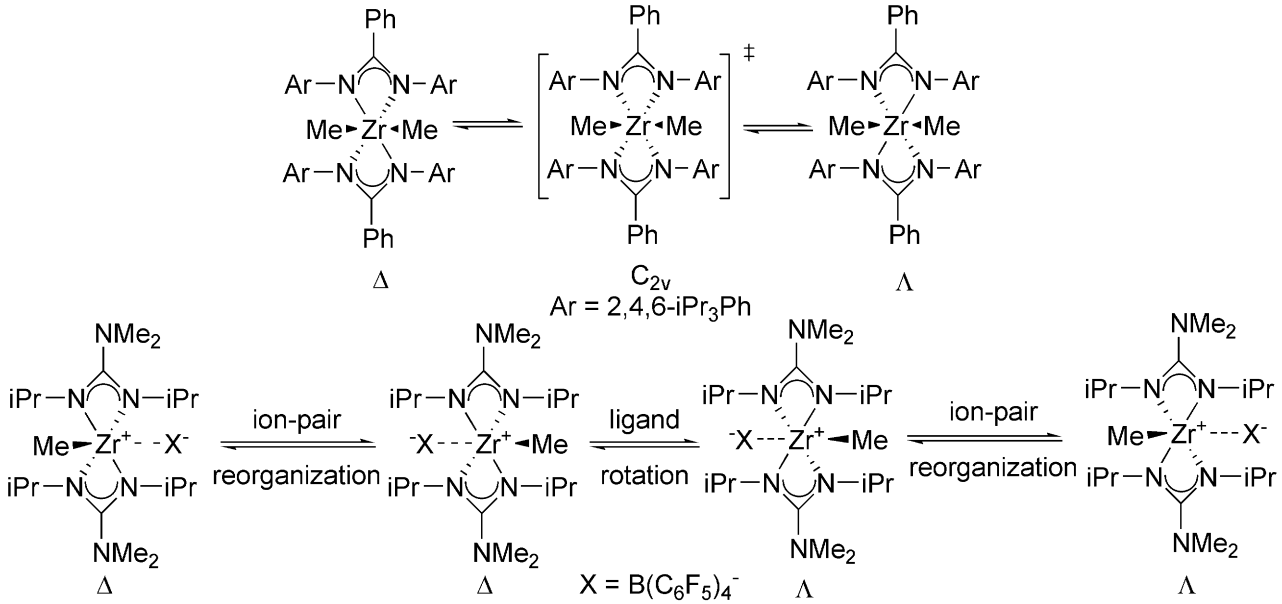
The vast majority of work involving propylene polymerization using group 4 [$RC(NR'_2)$] complexes has been reported by Eisen and co-workers [45,46]. The focus of much of this research has centered on propylene polymerization using bis-[$RC(NR'_2)$] complexes featuring achiral or chiral [$RC(NR'_2)$] ligands. This is understandable as the *cis*-octahedral complexes are chiral and upon activation could provide stereoregular polypropylene (PP). Almost all of these studies employed activation with MAO though more recent work has examined the use of discrete activators. The reader is referred to a recent review for more details [2] – a brief summary of this work is provided here.

In essence, complexes of this type do furnish stereoregular (isotactic) PP upon activation with MAO but generally only at high *P* and usually at rates that are 10^2–10^3 lower than chiral *ansa*-metallocene complexes. At lower *P* (or *T*) the PP formed consists of an elastomeric fraction and a stereoregular fraction. The elastomeric fraction differs in MW from the stereoregular fraction though both may have a Schulz-Flory MWD (PDI ~ 2). These catalysts isomerize higher α-olefins [45g] and there is evidence through D-labeling studies, of chain-end epimerization occurring during polymerization of propene [45b]. However, it is now thought in the case of Ti, that the isotactic fraction is produced by a chiral, cationic $[RC(NR'_2)_2]_2TiR$ complex, while the elastomeric fraction is formed *via* ligand abstraction/modification of the former, to furnish a $[RC(NR'_2)_2]TiR_2$ catalyst (Scheme 4) [45c]. A complicating feature is that both complexes are susceptible to reduction in the presence of excess MAO [45c], and one suspects, at least in the latter case, that the resulting Ti(III) complex may also be reactive towards polymerization (*cf.* Table 1, entry 27) [27].

In the case of Zr, the situation is less clear. Based upon polymerization experiments with MAO vs. BR_3 at elevated *T* and *P* it was originally concluded that a cationic $[RC(NR'_2)_2]_2ZrR$ complex was responsible for formation of isotactic PP [45g]. However, more recent work showed that the ion-pair formed from $[RC(NR'_2)_2]_2ZrMe_2$ and [Ph_3C][BR_4] was *inactive* towards propene at room *T*; only upon addition of small quantities of MAO (50:1 Al:Zr) was very high activity seen (i.e. 10^7 g PP mol Zr^{-1} h^{-1} vs. 10^5 g PP mol Zr^{-1} h^{-1} upon activation with a large excess of MAO) [45d]. Reduction to Zr(III) was observed during addition of MAO to the ion-pair, but exposure of the mixture to propene resulted in consumption of this intermediate. The PP formed (in liquid propene at room *T*) had the same (low) tacticity as the PP formed upon activation with excess MAO. However, the MW of the polymer was lower by a factor of nearly 10 – with PDI ~ 2 in both cases. The authors' argument that the same – i.e. a $[RC(NR'_2)_2]_2ZrH^+$ vs. $[RC(NR'_2)_2]_2ZrR^+$ complex is ultimately responsible is hard to



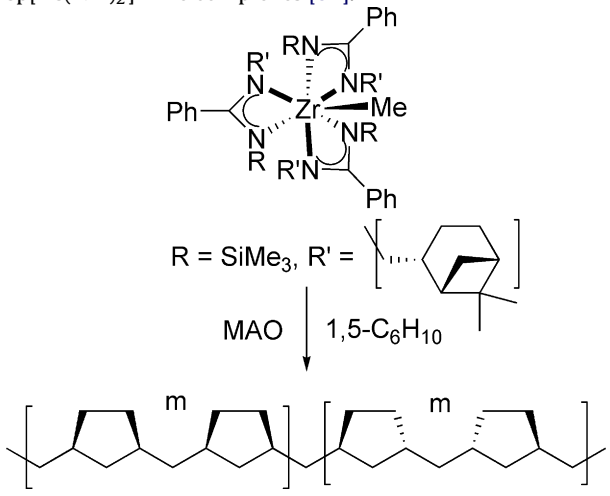
Scheme 4.



Scheme 5.

accept given this difference; perhaps ligand modification is also involved – the ion pair formed using $[Ph_3C][BR_4]$ was not structurally characterized so its structure is uncertain. It should be noted that studies of analogous bis(guanidinate) or bis(amidopyridine) Zr complexes revealed that the otherwise thermally stable ion-pairs (which have the expected structure) are susceptible to reaction with AlR_3 [24,33], giving rise to multi-site behavior during ethylene polymerization.

In addition to propene, the cyclopolymerization of 1,5-hexadiene has been studied by Eisen and co-workers using $[PhC(NTMS)_2]_2MMe_2$ (M = Ti, Zr) and a chiral, tris–$[RC(NR')_2]$ZrMe complex [6]. All of these catalysts afforded poly(methylenecyclopentane) (PMCP) upon activation with excess MAO. The most active catalyst (A = 27 kg PMCP mol Zr^{-1} h^{-1} at 25 °C) was the tris–$[RC(NR')_2]$ complex, which furnished oligo-PMCP (X_n < 40) with about 60–70% *trans* cyclopentane rings, with the *cis* and *trans*-rings arranged in a predominantly *meso*-fashion. The microstructure of the PMCP formed differed from that observed using achiral or chiral metallocene catalysts [47]. It should be noted in connection with this work, that Sita and co-workers had earlier reported the living cyclopolymerization of 1,5-hexadiene to furnish higher MW, *trans*-PMCP using achiral $Cp[RC(NR')_2]$ZrMe complexes [3v].

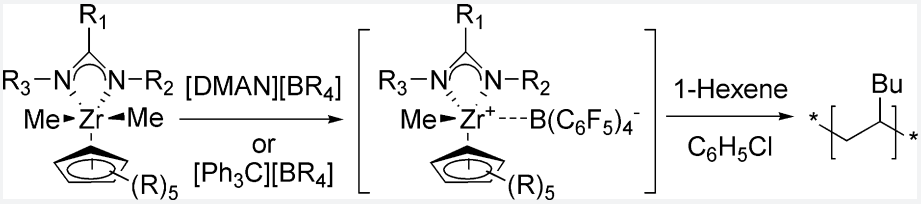


The dynamics of hindered bis-$[RC(NR')_2]$ catalyst precursors have been thoroughly studied by Hessen and co-workers, who showed that these isomerize *via* a trigonal twist mechanism with $\Delta H^{\ddagger} = 47.8 \pm 1.0$ kJ mol^{-1} and $\Delta S^{\ddagger} = -32.8 \pm 4.1$ J mol^{-1} K^{-1} (Scheme 5) [26]. In less hindered complexes, such as the bis-guanidinate complexes studied by Arnold and Bergman, this or a related process, such as ligand rotation about the C—Zr axis, is slow on the NMR time scale at 220 K [24]. On the other hand, given the configurational stability of cationic, chiral $Cp[RC(NR')_2]ZrR^+$ complexes with respect to ligand rotation (*vide infra*) [3] it is less clear that racemization of the active species involved in propene polymerization is as facile. In the work of Arnold and Bergman [24], the ion-pair formed using $[Ph_3C][BR_4]$ was fluxional at room temperature, indicating that both ligand rotation and ion-pair reorganization processes were rapid (one signal for the iso-propyl Me groups). At 188 K, four Me signals were observed; this behavior is consistent with rapid ion-pair reorganization but slow racemization due to ligand isomerization (by either a trigonal twist or rotation mechanism). At least in this case, it is not obvious that, e.g. i-PP should be produced by a site control mechanism, unless the growing polymer chain (or the bulky aluminoxane counter-ion [43]) impedes racemization at elevated T. Further work into these issues is clearly warranted; the one configurationally stable and chiral member of this class of compounds, namely a biaryl-bridged, or *ansa*-bis(amidopyridine)Ti complex, was only studied for its activity in ethylene polymerization [31,48].

1.1.5. Living olefin polymerization using group 4 amidinate complexes

The first reports of living and stereoregular 1-hexene polymerization using group 4 $Cp[RC(NR')_2]$ complexes by Sita and co-workers were quite surprising, especially in view of earlier work on Cp $[RC(NR')_2]$ complexes, where, at least upon activation with MAO, the catalysts were distinctly non-living [7,14] while discrete ion-pairs appeared to have limited stability in halogenated or aromatic solvents [37]. However, over the ensuing 10 years additional work from the Sita group has shed some light on this apparent dichotomy. Listed in Table 2 are various ion-pairs and their performance in 1-hexene polymerization in chlorobenzene solution at or above −10 °C. It can be seen that

Table 2
Living 1-hexene polymerization using Cp[RC(NR′)$_2$] initiators.

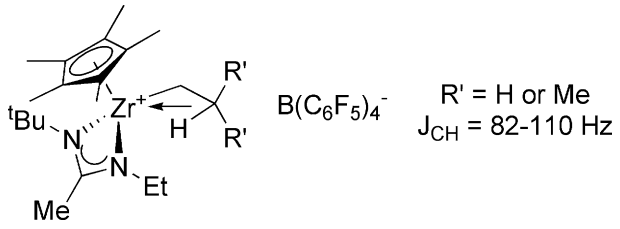


Entry	R	R_1	R_2	R_3	T (°C)	M_n (PDI)	Comments	Ref.
1	Me	Me	Cy	Cy	0	11,000 (1.10)	Atactic	[3w]
2	Me	Me	Et	^{t}Bu	−10 to 25	49,200 (1.03)–32,600 (1.50)	Isotactic	[3w]
3[a]	Me	Me	Cy	^{t}Bu	−10	14,000 (1.03)	PMCP (82% *trans*)	[3v]
4	Me	Me	Et	^{t}Bu	−10	19,800 (1.03)	Isotactic	[3k]
5	Me	H	Et	^{t}Bu	−10	20,100 (1.59)	Isotactic (II < entry 4)	[3k]
6	Me	Ph	Et	^{t}Bu	−10	19,300 (1.02)	Isotactic (II < entry 5)	[3k]
7	Me	^{t}Bu	Et	^{t}Bu	−10	–	Inactive	[3k]
8	Me	H	^{i}Pr	^{i}Pr	−10	25,100 (1.23)	Atactic	[3k]
9	Me	Me	Et	^{t}Bu	−10	19,800 (1.03)	Isotactic	[3p]
10	Me	Me	^{i}PrCH$_2$	^{t}Bu	−10	7940 (1.03)	Atactic 57% conversion	[3p]
11	Me	Me	^{t}BuCH$_2$	^{t}Bu	−10	–	Inactive	[3p]
12	Me	Me	PhCH$_2$	^{t}Bu	−10	19,300 (1.10)	Isotactic	[3p]
13	Me	Me	*o*-Cl-PhCH$_2$	^{t}Bu	−10	–	Inactive	[3p]
14	Me	Me	3-Me-PhCH$_2$	^{t}Bu	−10	23,600 (1.48)	Isotactic, unstable	[3p]
15	Me	Me	MesitylCH$_2$	^{t}Bu	−10	–	Inactive, unstable	[3p]
16	H	Me	^{i}Pr	^{i}Pr	−10	20,800 (1.03)	Atactic	[3u]
17	H	Me	Cy	Cy	−10	23,500 (1.06)	Atactic	[3u]
18	H	Me	Cy	^{t}Bu	−10	21,700 (1.09)	Atactic	[3u]

[a] Polymerization using 1,5-hexadiene, forming poly(methylenecyclopentane) (PCMP).

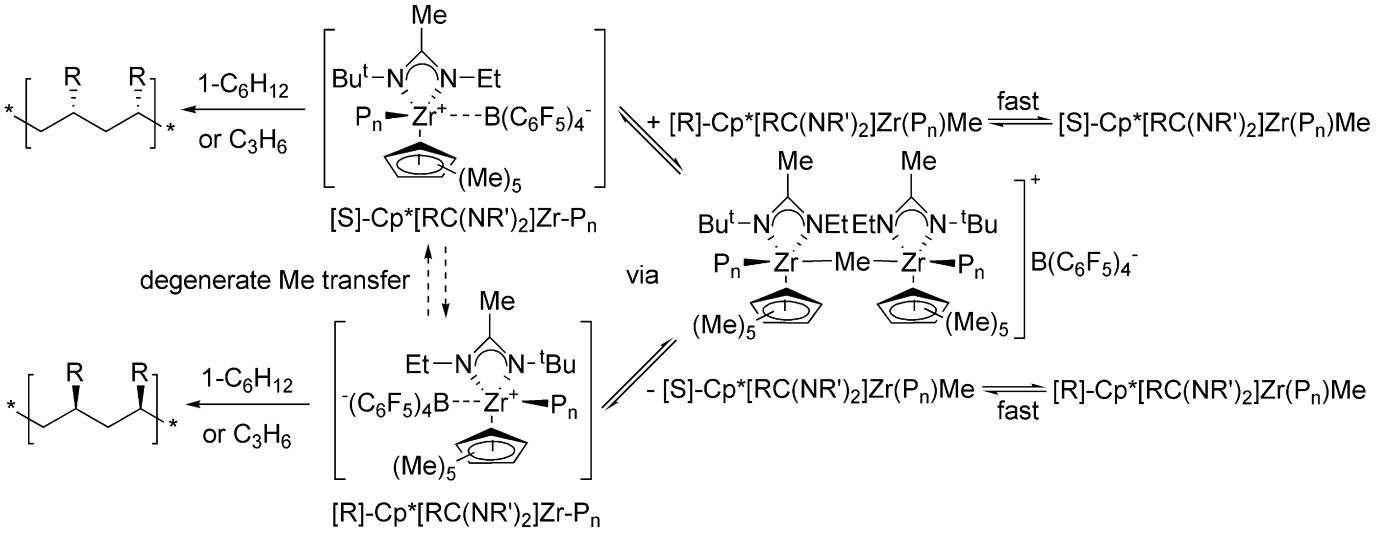
the principle difference here involves the use of complexes with N-alkyl vs. N-SiMe$_3$ substituents. Since the size of a SiMe$_3$ group is roughly equivalent to ^{i}Pr or Cy, we suspect the lower stability of the former ion-pairs reflects electronic differences or possibly the ease of C–H activation of SiMe$_3$ groups vs. alkyl substituents.

Most of the published work has focused on the Cp* complexes (entries 1–3) where the efficacy of these complexes as initiators of living 1-hexene polymerization initially appeared largely unaffected by the nature of the groups R_2 and R_3. Isotactic polymer was formed only if there was a large difference in size between these two substituents (i.e. R_2 = Et vs. ^{t}Bu). On the other hand, the living character of the polymerization is strongly affected by the central substituent (entries 4–7 with R_1 = H < Me ∼ Ph) with the most hindered complex (entry 8, R_1 = ^{t}Bu) being inactive. Where R_1 = H the diminished living character seems to be due to a higher tendency of the ion-pair towards reaction with the halogenated solvent. Surprisingly, the tacticity of the polymer formed was also affected (isotacticity highest for R_1 = Me > H > Ph). The differences seen were attributed to buttressing effects of the central substituent on R_2 vs. R_3. Finally, branching at the β-position of R_2 appears to influence the results obtained (entries 9–11) with the neo-pentyl derivative being inactive and the i-Bu derivative being of lower reactivity than for R_1 = Et. For benzyl substituted complexes, both steric and electronic effects appear important where halogen coordination to the metal (entry 13) or C–H activation processes (entries 14 and 15) interfered with living polymerization. In the case of entry 15, one suspects the steric effect of the mesityl group must be similar to that of ^{t}Bu as both of these complexes were inactive, even if the former was unstable towards C–H activation. For the less hindered Cp complexes (entries 16–18), polymerization activity is enhanced, but applications of these initiators appears restricted to homo- or co-polymerization of sterically hindered monomers such a vinylcyclohexane or cyclopentene [3a,u].



The study of model complexes has revealed the sensitivity to steric effects. In essence, in [Cp*[RC(NR′)$_2$]ZrR][B(C$_6$F$_5$)$_4$] ion-pairs when R has β-H atoms, the alkyls are indefinitely stable at −10 °C due to strong β-H agostic interactions with the metal center [3h]. However, for systems with branching at the δ-position (as in living polymeryl chains), the ion-pairs feature lower stability in the absence of monomer and do not adopt agostic structures in solution. So, the living polymerizations observed result from rapid insertion vs. slow β-H elimination where this process appears reversible, and can result in chain-end epimerization, but not necessarily, chain transfer. One suspects that β-H transfer to coordinated monomer is even less facile due to the sterically hindered nature of many of these complexes [49].

In fact, recent work using MAO-activated complexes at 25 °C (which are not living polymerizations) [50] suggest that the principle mode of chain transfer does involve β-H elimination as the number of vinylidene end groups, with respect to main chain resonances, decreased significantly with increasing monomer concentration over the range studied. There was no evidence for chain transfer to Al (in MAO treated with BHT so as to remove AlMe$_3$) nor β-Me elimination, with 2,1-insertion of propene followed by β-H elimination, an important pathway limiting chain growth. Finally, the principle stereo-defect arises from enantiofacial mis-insertion of propene rather than competing chain end epimerization, or bimolecular exchange of growing chains.



Scheme 6.

A surprising feature of these polymerizations is that they are unimpeded in the presence of neutral dimethyl precursor, even though the expected μ-Me dinuclear complexes are formed. In fact, formation of these types of complexes appears freely reversible and rapid compared to chain growth, at least for certain combinations of complexes and monomers. Since the chiral ion-pairs are configurationally stable with respect to amidinate ligand rotation at low *T*, while the dormant, neutral dialkyls (or dinuclear complexes?) are not, tacticity can be eroded through degenerate methyl group transfer in the presence of excess dialkyl (Scheme 6) [3o]. The process can be exploited to make tactic–atactic block or stereogradient copolymers of propene by metering in activator, (in one portion or continuously) and/or the same (or a different) dialkyl, so as to form tri- or higher blocks [3f,g].

A more important, recent development concerns the use of reversible chain transfer to added $ZnEt_2$ [3c,e]. Since the cationic amidinate complexes are true living polymerization initiators at low *T*, one does not need exchange to be rapid compared with propagation, as in quasi- or non-living systems (i.e. chain shuttling polymerization or metal-catalyzed chain growth on Zn [51]). Thus, in this case, it should be possible to form blocky homo- or co-polymers *with narrow MWD* using suitable combinations of amidinate complexes and $ZnEt_2$, and where the total number (and MW) of chains formed is dictated by the concentration of added chain transfer agent.

As previously mentioned the polymerization of hindered monomers, as well as cyclopolymerization of α,ω-dienes to form stereoregular polymers [3a,c,v] using these initiators has been investigated, while a recent report [52] indicates that 4-methylpentene can also be polymerized in an isotactic manner using the Cp[RC(NR′)$_2$] complexes.

This class of complexes holds great promise for the controlled and economical synthesis of blocky copolymers, provided the tacticity of the poly(propylene) formed can be increased to a useful level. Though highly tactic poly(1-hexene) is produced, the stereoselectivity of propene insertion is fairly low, corresponding to $\beta = 0.89$ at 25 °C ([*mm*] ~70%) [50]. Thus, the melting *T* of crystalline blocks is lower than anticipated. No doubt, with suitable adjustment of steric hindrance at the metal this limitation can be overcome.

1.1.6. Group 4 amidinate vs. metallocene catalysts

In the introduction, it was stated that amidinate ligands can be considered sterically equivalent with cyclopentadienyl but isoelectronic with π-allyl ligands. The cone angles of unhindered amidinate ligands and cyclopentadienyl can be considered nearly equivalent at least in the plane of the chelate ring, while some of the most hindered amidinate ligands having 2,6-di- or 2,4,6-tri-isopropylphenyl groups exceed the cone angle of Cp* in both principal dimensions (i.e. in- vs. out-of-plane of the chelate ring).

However, for unhindered complexes such as those studied by Sita and co-workers, it should be borne in mind that the amidinate ligand is relatively unhindered above and below the plane of the chelate ring. Further, it is clear that a single [RC(NR′)$_2$] ligand will never occupy more than two coordination sites on a transition metal. Thus, in my view, these ligands provide less steric stability than a cyclopentadienyl ligand of otherwise similar dimensions, and the complexes formed from the [RC(NR′)$_2$] ligand can be viewed as coordinatively unsaturated.

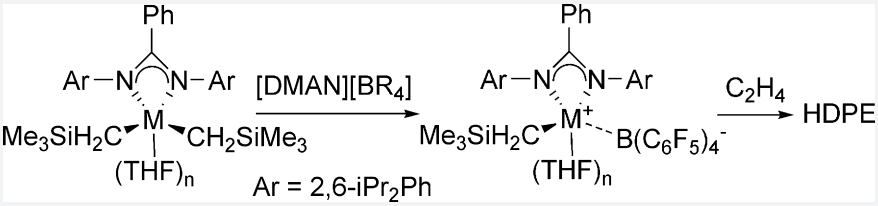
As for the electron count, the amidinate ligand is formally a 3e donor and for late metal or d^n complexes that is certainly appropriate. However for early metal, d^0 complexes, one has to consider π-donation from the remaining lone pair on N as being important, though not nearly as developed as in the case of amido groups based on M–N distances. In addition, the pK_A of simple amidines {the pK_A of Ph(=NH)NH$_2$ is 26.7 in DMSO [53]} far exceeds that CpH, and Cp*H, implying that these ligands are electron rich σ-donors.

In reviewing the available evidence, this somewhat unique combination of steric and electronic properties appears to stabilize higher alkyls towards β-H elimination or chain transfer to monomer, though at the expense of reduced insertion rates when compared with metallocene complexes. As to which of these properties is the more important awaits further, definitive research.

1.1.7. Olefin polymerization using other early transition metal amidinate complexes

Since the original reports on the use of group 4 [RC(NR′)$_2$] complexes in olefin polymerization, publications and patents on the use of other early transition metal amidinate complexes have appeared. Most of the activity has focused on neutral group 3 complexes, which are isoelectronic with cationic group 4 amidinate complexes, but applications to ethylene polymerization and selective oligomerization using group 5–6 catalysts have also appeared. To my knowledge, there has not been a single report of olefin polymerization using a group 7 metal, though such compositions are sometimes claimed in patent applications, etc.

Table 3
Ethylene polymerization using $[RC(NR')_2]Y$ complexes.[a]



Entry	M	*n*	TIBAO:Y	*T* (°C)	*t* (min)	Activity	M_w (PDI)	Ref
1	Y	1	0	50	5	1.03×10^6	430,000 (1.2)	[56c]
2	Y	1	0	50	10	0.79×10^6	644,000 (1.2)	[56c]
3	Y	1	0	50	20	0.46×10^6	854,000 (1.2)	[56c]
4	Y	1	0	50	30	0.40×10^6	1,270,000 (1.1)	[56c]
5	Y	2	0	50		Inactive		[56c]
6	Y	2	10:1	50	5	2.67×10^6	361,000 (2.1)	[56c]
7	Y	2	10:1	50	20	1.15×10^6	689,000 (1.9)	[56c]
8	Y	1	0	50	20	0.46×10^6	854,000 (1.2)	[56a]
9[b]	Y	1	0	50	20	Inactive		[56a]
10[b]	Y	1	0	80	20	0.35×10^6	126,000 (1.7)	[56a]
11	Y	1	10:1	50	20	1.15×10^6	689,000 (1.9)	[56a]
12[b]	Y	1	10:1	50	20	1.25×10^6	213,000 (2.5)	[56a]
13	Sc	1	20:1	30	20	2.40×10^4	93,000 (1.6)	[56b]
14	Y	2	20:1	30	20	3.00×10^6	1,670,000 (2.0)	[56b]
15	La	2	20:1	30	20	1.40×10^4	470,000 (2.5)	[56b]

[a] Toluene solvent, 5 bar ethylene unless otherwise noted.
[b] Ph = C_6F_5.

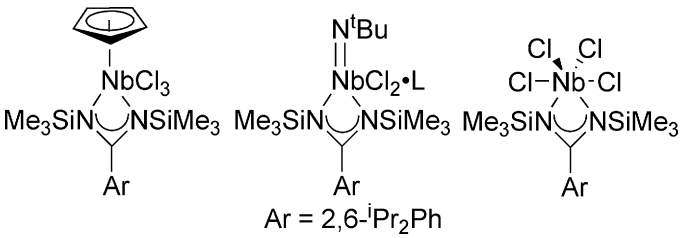
1.1.7.1. Olefin polymerization using group 3 amidinate complexes. The initial report in this area was not encouraging [54]; isoelectronic but dinuclear $\{[PhC(NSiMe_3)_2]_2YH\}_2$ hydrides polymerized ethylene at low activity (~57 g PE mol Y^{-1} h^{-1} bar^{-1} at 55 °C) and furnished PE with a broad MWD (M_w = 240,000, PDI = 5.2). These and the alkyl complexes studied had a high tendency towards C–H bond activation vs. insertion processes. Analogous guanidinate complexes $\{[(Me_3Si)_2NC(N^iPr)_2]_2YH\}_2$ were significantly more active (442 kg mol Y^{-1} h^{-1} bar^{-1}) [55].

Work on sterically hindered mono-amidinate complexes was much more promising [56]. Upon activation with $[PhNHMe_2][BR_4]$ the cationic complexes polymerized ethylene at high activity and furnished PE with a narrow MWD at elevated T (Table 3). When using aluminoxane scavengers such as tetra-i-butyldialuminoxane (TIBAO), PE with a Schulz-Flory MWD was produced at high activity consistent with effective chain transfer to Al. The mono-amidinate dialkyls bind 1 or 2 equiv. of THF. The latter complexes are inactive for polymerization, though the coordinated THF can be scavenged using TIBAO. In a more electron deficient complex (Ph = C_6F_5), THF binding was sufficiently strong that the mono-THF adduct was only active at higher T or upon activation in the presence of TIBAO. Finally, Sc and La complexes were about 2 orders of magnitude less active than the Y complex, while the productivity of lanthanide derivatives depended on ionic radius [56b].

Related work has been reported using sterically hindered, mono-APy complexes of Y [57]. The activity of these complexes is a sensitive function of steric hindrance, while the MW and MWD are dependent on the presence of TIBAO as well as *T*. Detailed studies reveal that the yttrium dialkyls, upon activation with $[R_3NH][BR_4]$ effect quasi-living polymerization by catalyzed chain growth on Al [51a]. Precipitation of the polymer at sufficiently high MW complicates the behavior of these complexes, as reversible chain transfer to Al is subsequently impeded by the insolubility of both living and dormant chains. Interestingly enough, these same dialkyls can be activated for ethylene polymerization through reaction with either H_2 or silanes [57b]. Trinuclear hydride complexes $[\{(APy)Y\}_3(\mu^2\text{-}H)_3(\mu^3\text{-}H)_2(CH_2SiMe_3)(THF)_2]$ are thought to be the active species in this case.

1.1.7.2. Olefin polymerization using group 5 amidinate complexes. Most of the synthetic and mechanistic work in this group has focused on Ta(V) complexes (*vide infra*), though $[PhC(NSiMe_3)_2]V(III)Cl_2$ or related complexes, are also very active catalysts when supported on $MgCl_2/Al(OR)_{3-n}R_n$ (A = 1.49–3.12 × 10^6 g PE mol V^{-1} h^{-1} bar^{-1} at 50 °C) [58]. Single site behavior is observed (M_w = 762–747 K with PDI = 2.0), though the structure of the supported catalyst is unknown. The corresponding soluble complexes show lower activity (2.42–3.73 × 10^5 g PE mol V^{-1} h^{-1} bar^{-1} at 50 °C) when activated by $AlEt_2Cl$ in toluene solution but, also produce high MW polymer (M_w = 220–1600 K with PDI 2-10, depending on conditions) [59b]. On the other hand, a neutral bis-$[RC(NR')_2]$ complex $[PhC(NSiMe_3)_2]_2V(III)Me$ is barely active in ethylene polymerization [59a] though an analog featuring electron deficient ligands (Ph = C_6F_5) [59c] shows improved performance (ca. 2 kg mol V^{-1} bar^{-1} h^{-1} at 80 °C) while both complexes produce low MW oligomers with a Schulz-Flory length distribution.

Initial reports from the group of Leskela featured the high polymerization activity of unhindered $(APy)_2TaCl_3$ [APy–H=2-$PhCH_2NH$–C_5H_4N:, 2,6-$(PhNH)_2$–C_5H_3N:] complexes upon activation with MAO (2000:1, A = 0.16–4.78 × 10^6 g PE mol Ta^{-1} h^{-1} bar^{-1} at 30–80 °C). Though single site behavior was observed (M_w = 201–66 K with PDI = 1.8–2.5), the catalysts were unstable at elevated *T* and the structure of the active catalyst was not elucidated [12,60]. A later report on the use of a $Cp^*[MeC(N^iPr)_2]TaCl_3$ complex showed lower activity upon activation with MAO (4.7 × 10^5 g PE mol Ta^{-1} h^{-1} bar^{-1} at 60 °C) [61] and again single-site behavior (M_n ~80 K, PDI = 1.85). Surprisingly, activation of the corresponding trimethyl derivative with either $B(C_6F_5)_3$ or $[(Et_2O)_2H][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ did not lead to an active catalyst. More recent work from the group of Kempe using sterically hindered $(APy)_2TaCl_3$ or $(APy)_2TaMe_3$ (APy–H=2-[2,6-$^iPr_2C_6H_3NH$]C_5H_4N:) complexes revealed very low activities (5–16 × 10^3 g PE mol Ta^{-1} h^{-1} bar^{-1} at 60–80 °C) for ethylene polymerization upon activation with MAO, or $[R_3NH][B(C_6F_5)_4]$, while the ion-pair derived from the trimethyl complex and $B(C_6F_5)_3$ was unstable in solution [62].



The situation for Nb is similar; Green and co-workers evaluated [(2,4,6-$^{i}Pr_3C_6H_2$-C(NSiMe$_3$)$_2$]NbCl$_4$, and mono-^{t}Bu-imido or mono-η^5-Cp derivatives thereof in ethylene polymerization upon activation with MAO (Al:Nb 2400:1) [63]. Activities did not exceed 10^4 g PE mol Nb^{-1} h^{-1} at 2 bar and 25 °C. An (APy)$_2$NbMe(η^2-PhC≡CSiMe$_3$) (APy–H=2-Me$_3$SiNH-6-Me-C$_5$H$_3$N:) complex, which is formally Nb(III), gave a stable ion-pair upon activation with B(C$_6$F$_5$)$_3$ [64]; the ion-pair was active for ethylene polymerization (4.4 kg PE mol Nb^{-1} h^{-1} at 80 °C and 6.5 bar) and furnished PE with a narrow MWD (M_p 36,000 with PDI = 1.8).

The picture that emerges from the limited number of studies conducted is that generally speaking [RC(NR′)$_2$] complexes of group 5 offer little advantage over those of groups 3 or 4, while activation with MAO can lead to different results compared to discrete activators.

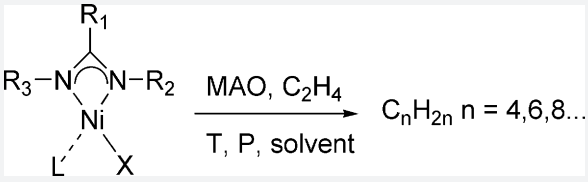
1.1.7.3. Olefin polymerization using group 6 amidinate complexes. Though amidinate complexes of all the group 6 elements have been reported in the literature, and there are a few reports on the chemistry of Cr(III) alkyl derivatives [65], applications to olefin polymerization have focused only on Cr and have appeared exclusively in the patent literature. The first such example featured the use of a silica supported [PhC(NSiMe$_3$)$_2$]$_2$Cr complex which when activated with either excess AlEt$_3$ or BuLi furnished high density PE with [η] = 5.8–12.3 dL g^{-1} at an activity of 1.97 kg mol Cr^{-1} h^{-1} bar^{-1} at 90 °C [9,10]. The nature of the supported catalyst was not disclosed. The first example using a soluble Cr(III) catalyst was reported by workers at Chevron where the complex [PhC(NSIMe$_3$)$_2$]$_2$CrCH$_2$SiMe$_3$ was generated *in situ* and used to oligomerize ethylene to a mixture of α-olefins (C$_4$–C$_{30}^+$) with high purity for each α-olefin (>98.7%) [66]. The productivity of this catalyst was about 2.26 kg C$_2$H$_4$ mol Cr^{-1} h^{-1} bar^{-1} at 70–75 °C while a Schulz-Flory distribution of chain lengths was obtained. A patent application from Symyx reports, or at least claims a large number of amidinate ligands, and reports mono-[RC(NR′)$_2$]Ni, -Co and -Cr complexes prepared from one of these ligands [*o*-Me$_2$NC$_6$H$_4$CH$_2$C(N^{i}Pr)$_2$]. Only Ni complexes were evaluated in olefin polymerization, and generally low activities were observed (*vide infra*) [67]. A patent application from DuPont, featured the synthesis of bis(amidinate) complexes of group 4, Y, V and Cr, in which the amidinate ligands were covalently linked at the central C atom [48]. The Y complex was inactive, the V complex was not studied (or no examples were included), while the Cr(III) complex –[–CH$_2$CH$_2$C(NAr)$_2$]$_2$CrCl (Ar=2,6-^{i}Pr$_2$Ph) afforded high density PE with a productivity of 2.84 kg PE mol Cr^{-1} h^{-1} bar^{-1} at 25 °C upon activation with excess MAO in 1,2,4-trichlorobenzene. Finally, norbornene was polymerized (48% yield after 12 h) without ring-opening using a [MeC(NCy)$_2$]$_2$CrCl complex activated with modified MAO at room temperature in toluene [68]. Evidently, at least in solution, the active state for polymerization is Cr(III) in agreement with extensive studies featuring related chelating ligands [69].

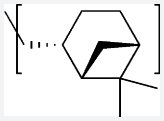
1.1.8. Olefin polymerization using late transition metal amidinate complexes

In comparison to the early transition metals, the use of late metal [RC(NR′)$_2$] complexes in olefin polymerization are quite restricted. This is not difficult to understand; in the case of a bis-[RC(NR′)$_2$] complex, a 14e metal alkyl (with a 16e olefin-alkyl as the resting state for a d^n metal [70]) requires that 7 of the total number of valence electrons should come from the metal, so that of the first row transition elements, a neutral Mn(III) for cationic Fe(IV) complex should be targeted for synthesis.

Neither oxidation state is particularly common for organometallic complexes of either metal, while the electron rich nature of these ligands is expected to lead to formation of lower oxidation state products through competing reduction of the metal. Thus, while stable [RC(NR′)$_2$]$_2$M(II) complexes are now known for the first row elements [71], attempts to prepare higher oxidation state late metal alkyls have been largely unsuccessful [72].

Table 4
Ethylene oligomerization using [RC(NR′)$_2$]Ni complexes.



Entry	R_1	R_2	R_3	L	X	Al:Ni	T (°C)	P (bar)	Solvent	TOF (h^{-1} bar^{-1})	Schulz-Flory α	Ref
1	Ph	$SiMe_3$	$SiMe_3$	L–X=κ^2-acac		200	25	30	Toluene	570	0.48	[78a]
2	Ph	$SiMe_3$	$SiMe_3$	L–X=κ^2-acac		200	25	30	CH_2Cl_2	1450	0.72	[78a]
3	Ph	$SiMe_3$	$SiMe_3$	L–X=κ^2-acac		200	70	30	CH_2Cl_2	2780	0.83	[78a]
4	Ph	$SiMe_3$	[a]	κ^2-TMEDA	κ^2-acac	200	25	30	Toluene	440	0.17	[78b]
5	Ph	$SiMe_3$	[a]	κ^2-TMEDA	κ^2-acac	200	25	30	CH_2Cl_2	980	0.14	[78b]
6	Ph	H		L–X=[RC(NR′)$_2$][b]		200	25	30	Toluene	550	0.69	[78c]
7	Ph	2,6-iPr$_2$Ph	2,6-iPr$_2$Ph	PPh_3	Ph	600	20	0.5	Toluene	920	0.57	[79]
8	p-tolyl	2,6-iPr$_2$Ph	2,6-Me$_2$Ph	PPh_3	Ph	600	20	0.5	Toluene	860	0.46	[79]
9	p-tolyl	2,6-iPr$_2$Ph	C_6F_5	PPh_3	Ph	600	20	0.5	Toluene	1040	0.56	[79]
10	p-tolyl	2,6-iPr$_2$Ph	C_6F_5	PPh_3	Ph	600	40	0.5	Toluene	1500	0.060	[79]

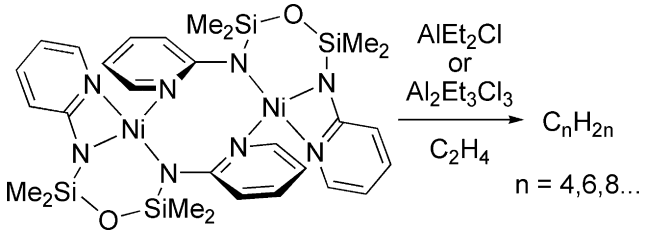
[a] R_3 = C(Ph) = CHSiMe$_3$; the precursor complex is octahedral.
[b] The precursor complex is dinuclear with four bridging [RC(NR′)$_2$] ligands.

Mono-[RC(NR′)$_2$] complexes have been reported for the later transition elements and some of these have been investigated for use in olefin polymerization. To my knowledge, there have been no reports on the use of group 8 complexes in olefin polymerization, though amidinate complexes of Ru have been employed in ATRP of methyl methacrylate; in this case the amidinate ligand bridges two Ru centers [73]. Similarly, for the group 9 metals, aside from a previously mentioned patent application where a Co [RC(NR′)$_2$] complex was reported but not evaluated [67], there is a single, isolated report on the use of a trinuclear Ir(pyridine-2-thiolate) complex in norbornene polymerization upon activation with MAO [74].

In fact of the late transition metals, only Ni, and Cu have been seriously investigated for this purpose. It should be mentioned though that a (APy)$_2$Pd complex (APy-H=4-Me-2-Me$_3$SiNH-C$_5$H$_3$N:) was active for condensation polymerization of a disilane (*vide infra*) [75].

1.1.8.1. Olefin polymerization using Ni amidinate complexes. *In situ* formation of [RC(NR′)$_2$]NiR(Py) complexes from a wide variety of [RC(NR′)$_2$] ligands, and (Me$_3$SiCH$_2$)$_2$Ni(Py)$_2$ was reported by workers at Symyx [67]. These mixtures were activated with a 3-fold excess of B(C$_6$F$_5$)$_3$ and upon exposure to ethylene, solid polymer was produced at an activity between 1.67 and 12.0 g PE mol Ni^{-1} h^{-1} at 3.4 bar and 25 °C. In one case, the complex [PhN(Ar)$_2$]NiCH$_2$SiMe$_3$(Py) (Ar=2,6-^{i}Pr$_2$-Ph) was isolated and subsequently activated with B(C$_6$F$_5$)$_3$. The activity was somewhat improved 74 g PE mol Ni^{-1} h^{-1} at lower pressure (1.5 bar) while no characterization of the PE was reported. Evidently, the material was of low MW and/or branched since part of it was soluble in toluene at room temperature.

The first literature report of ethylene polymerization using a Ni complex, involved activation of a *dinuclear* [(APy)$_2$Ni]$_2$ complex, featuring both chelating and bridging APy ligands [APy-H=O(2-SiMe$_2$NH-4-Me-C$_5$H$_3$N:)$_2$] with Et$_2$AlCl [76]. This formulation was active for ethylene oligomerization (TOF = 2400 mol C$_2$H$_4$ mol Ni^{-1} h^{-1}) and provided oligomers with a Schulz-Flory distribution, containing mainly internal C=C bonds. Using the more Lewis acidic Et$_3$Al$_2$Cl$_3$ as activator in CH$_2$Cl$_2$, highly branched oligomers were formed (TOF = 122,000 h^{-1}) which featured a narrow MWD (M_n = 230 with PDI = 1.14).



Since the Ni precursor contains no Ni–C bonds, evidently at least one of the APy ligands (per Ni) is susceptible to exchange with the alkylaluminum compound. It is interesting to note however that the oligomeric product(s) formed using Et$_3$Al$_2$Cl$_3$ were identical to those reported by Sen and coworkers using a [(π-methallyl)NiBr]$_2$ and AlCl$_3$ in CHCl$_3$, where initial insertion into, or reaction with the π-methallyl group, was observed [77]. It is therefore unclear whether *any* of the APy ligand was coordinated to Ni under the conditions reported by Kempe et al.

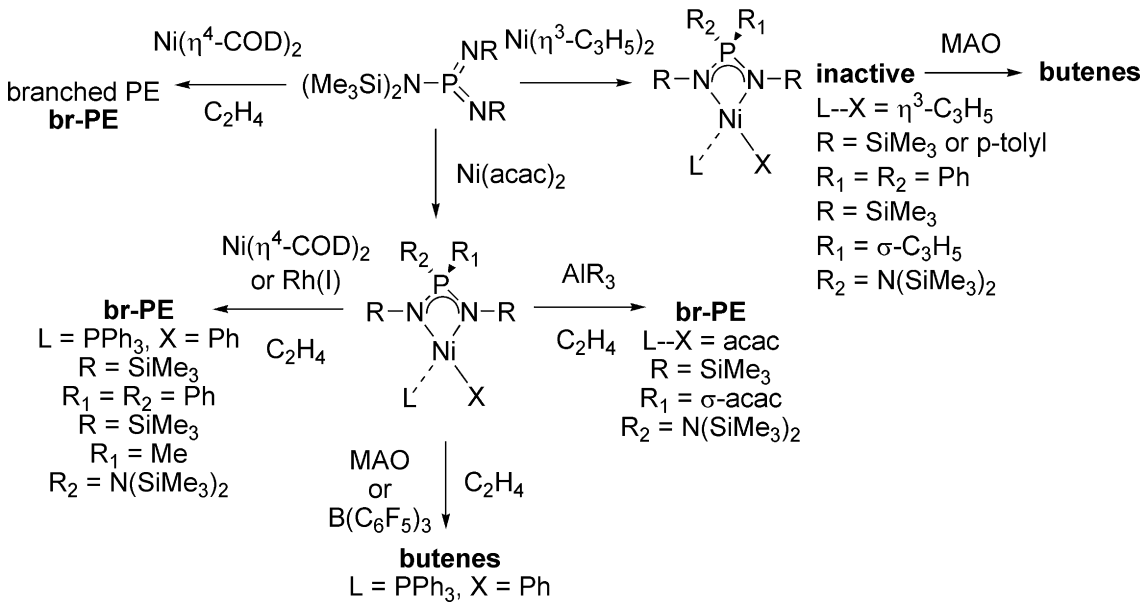
Eisen and co-workers reported ethylene oligomerization, propene dimerization and norbornene polymerization using mono(amidinate) complexes of Ni when activated with MAO [78]. The ethylene oligomer product distribution and activities observed were a function of *T* and solvent, in addition to the structure of the Ni catalyst precursor (Table 4). Generally speaking, the complexes produce mainly mixture of butenes and hexenes, though in one case in CH$_2$Cl$_2$ selectivity for higher oligomers was observed, which improved at higher *T* (entries 2 and 3).

More recently, a series of sterically hindered [RC(NR′)$_2$]NiPh(PPh$_3$) complexes were prepared and structurally characterized [79]. These PPh$_3$ complexes were unreactive towards ethylene, even in the presence of a 20-fold excess of Ni(COD)$_2$ at room temperature. On the other hand, in the presence of excess MAO, all complexes were active for ethylene oligomerization or norbornene polymerization. In ethylene oligomerization, all three complexes behaved rather similarly, with $\alpha \sim 0.5$–0.6. In one case, the selectivity for 1-butene improved to ca. 94% at elevated *T*, opposite to the behavior reported by Eisen. However, these results should not be that closely compared as the ethylene *P* were very different; TOF can be independent of, or show saturation behavior upon increases to ethylene *P* with late metal catalysts, while chain transfer rates can be significantly altered [80]. On the other hand, none of the complexes produced solid polymer as exemplified in the work reported by Symyx.

Though only oligomers are formed with simple α-olefins, these catalysts are useful for the synthesis of high MW, poly(norbornenes) (PNB), as are many other group 10 catalysts [81]. The discrete NiPh complexes provided PNB with productivities in excess of 10^7 g PNB mol Ni^{-1} h^{-1} while M_n varied from 82 to 376 kg mol^{-1} with PDI = 2.3–2.7 depending on catalyst and *T*. In contrast, the [RC(NR′)$_2$]Ni(acac) complex reported by Eisen was significantly less active (ca. 10^5 g PNB mol Ni^{-1} h^{-1}) and furnished somewhat lower MW polymer. Finally, the chiral bis-[RC(NR′)$_2$] complex [PhC(NSiMe$_3$)(N′-myrtanyl)]$_2$NiPy$_2$ upon activation with MAO also polymerized norbornene and with similar activity. However, the material formed was atactic (as were all the other samples) suggesting the chiral ligand had limited effects on the stereochemistry of insertion.

1.1.8.2. Olefin polymerization using Ni iminophosphonamide complexes. As mentioned in the introduction, Keim and co-workers reported ethylene polymerization using a catalyst formed from Ni(COD)$_2$ or Ni(η^3-allyl)$_2$ and the phosphorane (Me$_3$Si)$_2$NP(=NSiMe$_3$) at elevated *T* and *P*. The product was said to resemble low density PE in its properties. These authors inferred that the product formed from Ni(η^3-allyl)$_2$ and the phosphorane (Me$_3$Si)$_2$NP(=NSiMe$_3$), a [R$_2$P(NSiMe$_3$)$_2$]Ni(η^3-allyl) complex might be the active species [13a]. Subsequent work from the group of Fink established that Ni(COD)$_2$ and the phosphorane furnished chain-straightened, α-olefin oligomers at low *T* [82]. A group of scientists at Tosoh led by A. Yano established that the PE formed using this catalyst was branched, with a mixture of short (only Me) and long-chain branching (Hx$^+$). They also showed that active catalysts could be derived from Ni(II) salts, and the phosphorane in the presence of AlR$_3$ and related activators [83]. Subsequent work from the Fink group established that a [R$_2$P(NSiMe$_3$)$_2$]Ni(acac) complex was formed from the phosphorane and Ni(acac)$_2$ and that this complex could be activated for ethylene polymerization using AlEt$_3$ (Scheme 7) [13b].

Collins and co-workers prepared a number of discrete [Ph$_2$P(NR′)$_2$]Ni(η^3-allyl) complexes (R′ = SiMe$_3$, p-tolyl) including the mixture of diastereomers reported by Keim and co-workers [4e]. These complexes were *inactive* in ethylene polymerization under all conditions investigated, even though these workers could reproduce the results of Keim et al. when the phosphorane and Ni(η^3-allyl)$_2$ were reacted *in situ* in the presence of ethylene. It is suspected that the active catalyst is formed from the phosphorane and Ni(0)-diene impurities present in the bis-π-allyl Ni precursor, particularly at elevated *T*.



Scheme 7.

All of the complexes reported could be activated for ethylene oligomerization upon treatment with excess MAO under conditions similar to those reported by Eisen and co-workers. Activities were comparable (TOF ca. 5000–36,000 h^{-1} bar^{-1} depending on complex used) but higher selectivity for butenes was observed.

An unhindered $[Ph_2P(NSiMe_3)_2]NiPh(PPh_3)$ complex was prepared and characterized [4e]. It was essentially inactive for ethylene polymerization in the presence of a 10-fold excess of $Ni(COD)_2$ while it too furnished butenes at high activity on activation with excess MAO [or stoichiometric $B(C_6F_5)_3$]. However, in this case it was shown that $AlMe_3$ reacts by clean abstraction of the $[R_2P(NR')_2]$ ligand to furnish $[Ph_2P(NSiMe_3)_2]AlMe_2$ and a very unstable Ni(II) aryl–alkyl complex; presumably similar activation chemistry is involved using MAO. Finally, branched, oligo-PE was formed using a selective but, impractical PPh_3-scavenger, namely $(acac)Rh(C_2H_4)_2$.

Later work reported the synthesis of a more sterically hindered complex $[(Me_3Si)_2N(Me)P(NSiMe_3)_2]NiPh(PPh_3)$ [4b,c], analogous to that envisaged to form under the conditions reported by Keim, Fink and others. In this case, the phosphine ligand was more labile and branched PE with an *identical* microstructure to that reported by Yano and co-workers was produced in the presence of excess $Ni(COD)_2$, though this activator was not required to produce this material. The unusual branching distribution can be accounted for by chain-walking vs. insertion mechanism as revealed by DFT and kinetic modeling of polymer microstructure [4a,c].

Evidently, branched, higher MW PE is produced using a $[R_2P(NR')_2]Ni(L)R$ complex, while ethylene dimerization involves a so-called "naked" RNi(II)–L catalyst of undetermined structure. In view of the similarity in activation behavior reported for $[RC(NR')_2]Ni$ vs. $[R_2P(NR')_2]Ni$ complexes, it seems likely that similar conclusions apply as to the nature of the active species in the former case upon activation with MAO. It is still a matter of conjecture (or the predictability of DFT calculations [4a]) as to the ethylene polymerization behavior of a *bona fide* $[RC(NR')_2]NiR(L)$ species; the high-throughput experimentation of scientists at Symyx warrants closer scrutiny.

1.1.8.3. Olefin polymerization using Cu amidinate complexes. Although Cu amidinate complexes have been employed in the "insertion" polymerization of carbodiimides (*vide infra*) to our knowledge, their use in olefin polymerization has been restricted to reports in the patent literature [84]. Reaction of $CuCl_2$ with 2 equiv. of $PhC(=NSiMe_3)NHSiMe_3$ furnished a structurally uncharacterized Cu(II) complex formulated as $[PhC(NSiMe_3)_2]CuCl(L)$ ($L = \kappa^1$-$PhC(=NSiMe_3)NHSiMe_3$) on the basis of its IR spectrum and a combustion analysis. Upon activation with excess MAO, the complex furnished high density PE of high MW (M_w 820 K with PDI = 2.02). The productivity of this complex was 3.26 kg PE mol Cu^{-1} h^{-1} at 1 bar and 20 °C. A similar result was obtained using TIBAL instead of MAO. No further studies have been reported in the literature; it should be noted that other examples of Cu(II)-catalyzed ethylene polymerization have recently been shown to arise from formation of reactive $[(RC(NR')_2)AlR][MAO]$ complexes *in situ via* ligand abstraction [85].

1.2. Styrene and conjugated diene polymerization using transition metal amidinate complexes

As mentioned in Section 1, the polymerization of styrene or conjugated dienes using nucleophilic transition metal or lanthanide alkyls need not follow an insertion mechanism. Evidently, the formation of syndiotactic polystyrene (s-PSty) using, e.g. piano stool complexes of group 4 does involve insertion chemistry, and so reports on the use of transition metal $[RC(NR')_2]$ (or other) complexes for this purpose must be viewed as similar. On the other hand, formation of atactic polystyrene can occur by anionic, cationic and free-radical initiation – so these processes have to be carefully excluded before conclusions can be made.

With conjugated dienes the situation is more complicated. For example, many lanthanide complexes do furnish, e.g. poly(butadiene) (PBD) with high 1,4-incorporation, upon activation with main group metal alkyls, as do some late transition metals (e.g. Co and Ni). However, dienes are also susceptible to anionic polymerization and the polymers frequently do possess high 1,4-microstructure, at least in non-donor solvents; possibly lanthanide "ate" complexes may be in equilibrium with the corresponding main group metal alkyl and it is the latter that initiates polymerization?

In this review, we will not attempt to dissect these questions, since in most cases the data are not available to do so. The reader should bear these complexities in mind however in reviewing the available literature.

Historically, the first report of metal–[RC(NR′)$_2$] polymerization of dienes is that appearing in a patent dealing with the preparation of 1st row (Cr–Cu) transition metal 1,8-naphthyridine complexes [86]. Though the complexes themselves are simple, neutral coordination complexes, the Co complexes could be activated for diene polymerization using aluminum alkyls and furnished PBD with high (>85%) *cis*-1,4-microstructure. Given the non-innocent nature of these ligands, it seems plausible that they might be modified *in situ*. That this is likely, is evident from other studies in this patent, where vinyl chloride was polymerized using a variety of these complexes in the presence of aluminum alkyls or tri-isobutylborane; presumably free radication initiation is involved in this case, arising from either homolysis of metal alkyls and/or single electron reduction of the naphthyridine ligand.

The first examples of styrene polymerization featured discrete mono-[ArC(NR)$_2$]TiX$_3$ (Ar = Ph, R = SiMe$_3$, Ar = p-tolyl, and R = Me) complexes, which furnished syndiotactic polystyrene upon activation with MAO [21]. These complexes were of comparable activity to piano-stool complexes of group 4, but in some cases furnished more highly tactic polymer (85–95%). It should be noted that these, and some bis [RC(NR′)$_2$]MCl$_2$ complexes could also be activated for ethylene but not propene polymerization using excess MAO [21a]. Moreover, the corresponding dialkyls were inactive for ethylene polymerization in the presence of TIBAL and [Ph$_3$C][BR$_4$]. This initial report differs, in some important respects, from other reports on the same or similar complexes.

Subsequent work reported by Zambelli and co-workers focused on propylene, styrene and butadiene polymerization using a variety of [ArC(NR)$_2$]TiX$_3$ complexes at low *T* [87]. They observed that s-PP (∼50% *rr* triads), atactic PSty and trans-1,4-PBD (ca. 80% *trans*) were formed at −60 °C while s-PSty, *cis*-1,4-PBD and partially i-PP (40% *mm* triads) were produced at ambient *T*. In agreement with the findings of Eisen and co-workers, the latter material could be fractionated into isotactic and elastomeric PP differing in MW. The authors interpreted these findings by suggesting that a thermally unstable [(RC(NR′)$_2$)TiR$_2$][MAO] complex was responsible for production of s-PP, etc. at low *T*, and which disproportioned at higher *T* into a [(RC(NR′)$_2$)$_2$TiR][MAO] complex, with this being responsible for production of i-PP, and a [TiR$_3$][MAO] complex which gave rise to s-PSty, etc.

The problem with this conclusion, with the benefit of hindsight, is that it is now certain that a [CpTi(III)R][MAO] complex is responsible for s-PSty formation, at least when using piano-stool complexes of group 4. We can certainly account for the results by, e.g. invoking a formation of a [RC(NR′)$_2$]Ti(IV) complex at low *T* and a [RC(NR′)$_2$]Ti(III) complex at elevated *T*. This would certainly explain a change in tacticity and *cis*/*trans* ratio for PSty and PBD, respectively. Presumably, the conclusions of Eisen and co-workers then explain the results for PP (*vide supra*).

Two subsequent reports examined the activation of bis(guanidinate)- [88] and bis(pyrimidine- or pyridine-thiolate [89] complexes of Ti for styrene polymerization using MAO. In the latter case, s-PSty was produced using all complexes, though higher productivities were observed at lower *T* in some cases. A mono-pyridine-thiolate complex was also shown to produce s-PSty [90]. Unfortunately, the results reported for the bis(guanidinate) complexes are published in Chinese and no details are provided in the corresponding abstract. However, we suspect in both cases, a Ti(III)-[RC(NR′)$_2$]X complex is the active species involved.

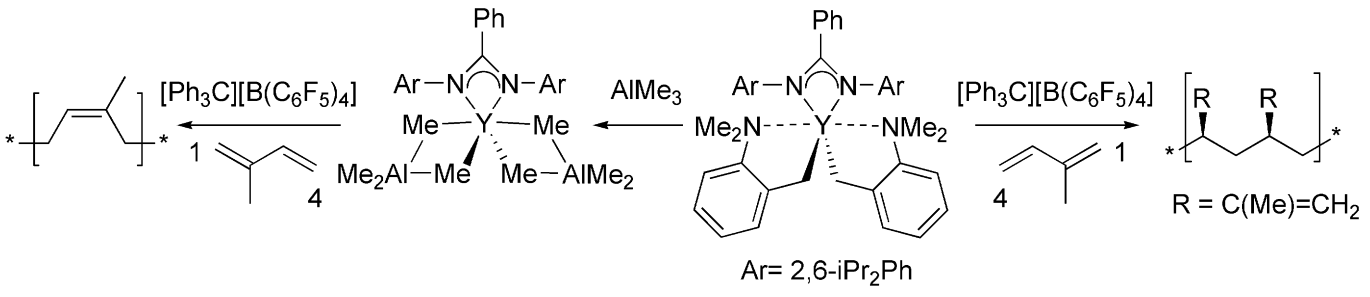
More recent work has focused on the use of discrete, [RC(NR′)$_2$] and [R$_2$P(NR′)$_2$] complexes of group 3 and the lanthanides for polymerization of butadiene and isoprene. Especially significant is the first report in which a sterically hindered mono-[RC(NR′)$_2$] complex of yttrium, upon activation with [Ph$_3$C][BR$_4$], affords highly isotactic, poly(3,4-isoprene) while in the presence of ≥3.0 equiv. of AlMe$_3$, a complete change in selectivity is observed, forming high MW *cis*-1,4 poly(isoprene) with better than 98% selectivity at −20 °C (Scheme 8) [91]. In the latter case, the trinuclear, Y/Al complex shown was implicated as the catalyst precursor.

Similar observations were made using sterically hindered (APy)Sc(CH$_2$SiMe$_3$)$_2$(THF) complexes (APy-H=6-Ar-2-Ar′NH-C$_5$H$_3$N: with Ar = TRIPP or Mes, and Ar′ = DIPP or Mes) [92]. Activation with [DMAN][BR$_4$] or [Ph$_3$C][BR$_4$] furnished isotactic, poly(3,4-isoprene) at low *T*, whereas modestly stereoregular *cis*-1,4-poly(isoprene) (≤90% *cis* at 20 °C) was formed in the presence of excess AlMe$_3$. Better results (i.e. 96% *cis*-1,4) were obtained using a bis(amido)Sc(APy) precursor and AlMe$_3$, presumably reflecting more efficient formation of a complex analogous to that shown in Scheme 8.

Analogous studies were reported using some less hindered group 3 and lanthanide [R$_2$P(NR′)$_2$] complexes – namely formation of poly(3,4-isoprene) on activation with [Ph$_3$C][BR$_4$] in the presence of TIBAL [93]. Some of the complexes polymerized isoprene in a quasi-living fashion under these conditions; surprisingly, the authors did not investigate the effect of AlMe$_3$ on these isoelectronic complexes, though they did invoke the participation of TIBAL in these polymerizations.

As far as can be ascertained, the polymerizations that give rise to isotactic, poly(3,4-isoprene) certainly involve a coordination mechanism since this microstructure is unknown for anionic, free radical or cationic polymerization mechanisms. Aside from the change in structure of the catalyst precursor, the reasons for the dramatic change in selectivity on addition of AlMe$_3$ are not completely understood. Presumably π-allyl intermediates are involved in 1,4-polymerization of dienes.

In summary, group 3 [RC(NR′)$_2$] or related complexes appear to hold great promise for the synthesis of *cis*-1,4-polyisoprene, which hopefully can supplement natural rubber in case of global



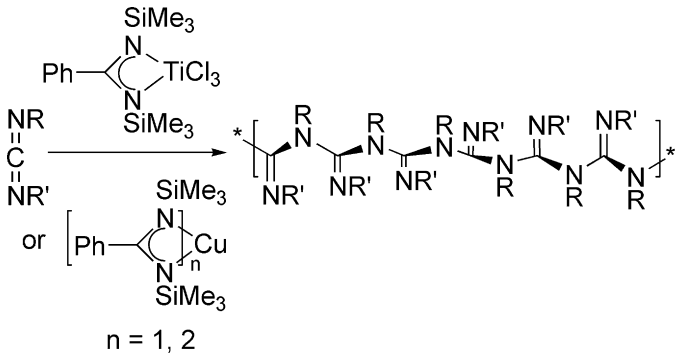
Scheme 8.

supply problems. As for s-PSty, this useful engineering thermoplastic continues to attract attention, despite diminished commercial production.

1.3. Polar monomer polymerization using transition metal amidinate complexes

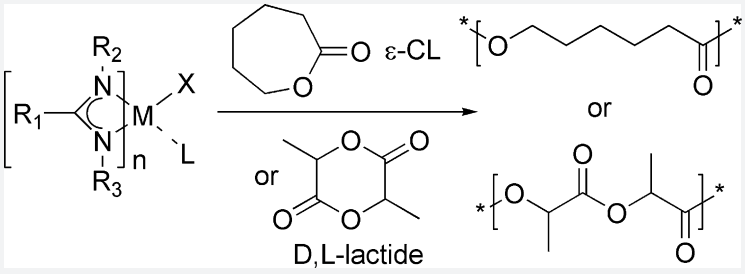
The first reports on the use of transition metal [RC(NR′)$_2$] complexes to polymerize functional monomers involves the seminal studies of Novak and co-workers on the use of group 4 [i.e. Ti(IV)] and group 11 [i.e. Cu(II) or Cu(I)] amidinate complexes for the controlled polymerization of carbodiimides [94]. This is a nucleophilic, addition polymerization with living characteristics where the metal complex exerts an effect on the helicity of the resulting polymer, when polymerizing chiral, carbodiimides. These materials have liquid crystalline properties and the 6,1-helical conformation which is important in developing a polar axis in this state, also persists in solution [95].

It is important to recognize that [RC(NR′)$_2$] ligands can be classified as hemi-labile, especially for low oxidation state, late transition metals, because the narrow bite angle results in reduced overlap with suitable acceptor orbitals on the metal. In addition, these are very weak π-acceptor ligands and there are also repulsive interactions with filled metal d orbitals. Presumably, coordination of the carbodiimide (*via* N), when coupled with this hemi-lability, leads to facile transfer of the metal from the initiator amidinate ligand to the growing chain.



In related work, (MeCp)$_2$M(N^{i}Pr$_2$) (M = Y, Er and Yb) complexes were shown to be effective for polymerization of PhN=C=O [96]. The first product formed in the case of Y was an κ^2-N,O-amidate complex resulting from nucleophilic addition of the amido group to PhN=C=O. Amidate complexes of this type are believed to be the initiators for ring-opening polymerization of lactams mediated by group 4 metallocene η^2-alkyne complexes; they could be generated from Cp$_2$M(η^2-RC≡CR″) (M = Ti or Zr) and caprolactam or β-propiolactam. In the case of Ti, the former reaction occurred with elimination of H_2 and coordinated alkyne to furnish a Cp$_2$Ti(κ^2-N,O-amidate) complex [97]. Finally, (MeCp)$_2$Y(κ^2-N,O-amidate) complexes, formed from the halide and N-lithiocaprolactam are also effective for ROP of ε-caprolactone (57–100% conversion at 60–80 °C with the formation

Table 5
ROP using transition metal [RC(NR′)$_2$] complexes.



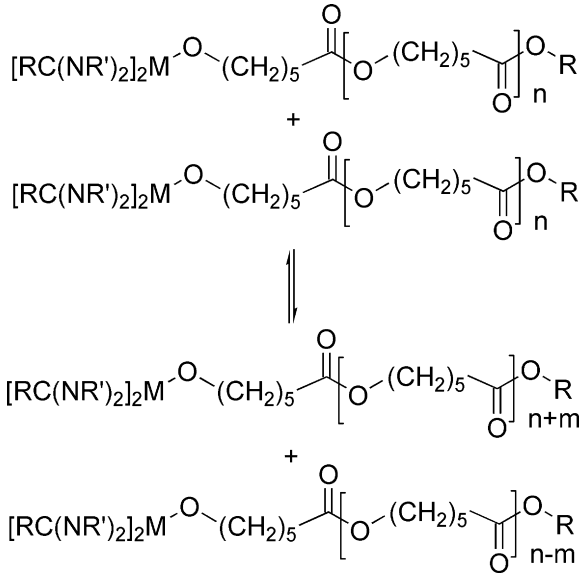
Entry	M	R_1	R_2	R_3	*n*	L	X	Mon	*T* (°C)	%Conv	M_n (K)	PDI	Ref
1	Y	Ph	$SiMe_3$	$SiMe_3$	2	–	OAr	D,L-LA	25	97	38.7	1.82	[99]
	Y	Ph	$SiMe_3$	$SiMe_3$	2	–	OBn	D,L-LA	25	96	57.7	1.50	[99]
2	Y	Ph	$SiMe_3$	$SiMe_3$	2	THF_4	OAr_2[a]	D,L-LA	25	28	6.7	1.71	[99]
3	Y	Ph	$SiMe_3$	$SiMe_3$	2	THF	O^{t}Bu$_2$[a]	D,L-LA	25	89	8.0	2.61	[99]
4	Y	p-tolyl	2,6-^{i}Pr$_2$Ph	2,6-^{i}Pr$_2$Ph	1	THF	[N(SiR$_3$)$_2$]$_2$	D,L-LA	25	97	58.7	1.50	[99]
5	Y	p-tolyl	2,6-Et$_2$Ph	2,6-Et$_2$Ph	1	–	[N(SiR$_3$)$_2$]$_2$	D,L-LA	25	74	33.6	1.72	[99]
6	Fe	Ph	$SiMe_3$	$SiMe_3$	2	–	$OCHPh_2$	ε-CL	25	100	36.4	1.20	[100]
7	Fe	Ph	$SiMe_3$	$SiMe_3$	2	–	$OCHPh_2$	D,L-LA	70	88	39.5	1.88	[100]
8	Nd, Gd, Yb (Y)[b]	Ph	Cy	Cy	3	THF_2	–	ε-CL	25	27–100	33.4–205	1.74–2.29	[101]
9	Y (Nd)	N(SiMe$_3$)$_2$	^{i}Pr	^{i}Pr	2	–	N^{i}Pr$_2$	ε-CL	25	86–100	79.9–228	1.78–2.36	[102]
10	Y (Lu)	N(SiMe$_3$)$_2$	^{i}Pr	^{i}Pr	2	–	H[c]	ε-CL	23	100	7.85–79.0	2.0–4.2	[103]
11	Y	Me	Me	Me	3	–	[d]	D,L-LA	25	100	53.1	1.84	[104]
12	Y (Yb)	Ph	$SiMe_3$	–$(CH_2)_3$–	6	DME	[d]	ε-CL	25	55–100	69.0–104	2.80–2.22	[105]
13	Y (Yb)	Ph	$SiMe_3$	–$(CH_2)_3$–	4	DME_3	[a]	ε-CL	25	57–73	32.3–41.1	2.41–2.50	[105]
14	Y (Nd, Lu)	N(SiMe$_3$)$_2$	^{i}Pr	^{i}Pr	2	–	OR (R = ^{i}Pr)	D,L-LA	25	51–98	6.4–9.7	1.12–1.50	[106]
15	Y (Nd, Sm, Lu)	N(SiMe$_3$)$_2$	^{i}Pr	^{i}Pr	2	–	OR (R = ^{t}Bu)	D,L-LA	25	55–93	7.7–9.3	1.22–1.64	[106]
16	Y (Nd, Lu)	N(SiMe$_3$)$_2$	^{i}Pr	^{i}Pr	2	–	OR (R = ^{i}Pr)	β-BL[e]	20	26–95	2.0–28.2	1.13–1.69	[106]
18	Y (Lu)	Cy	2,6-^{i}Pr$_2$Ph	2,6-^{i}Pr$_2$Ph	1	THF	$(CH_2SiMe_3)_2$	L-LA	70	91	33.6	1.20	[107]
19	Y (Nd, Lu)	Cy	2,6-Me$_2$Ph	2,6-Me$_2$Ph	1	THF_2	$(CH_2SiMe_3)_2$	L-LA	70	93	25.2	1.29	[107]
20	Y	Ph	2,6-Me$_2$Ph	2,6-Me$_2$Ph	1	THF_2	$(CH_2SiMe_3)_2$	L-LA	70	90	33.7	1.23	[107]
21	Y	Ph	2,6-^{i}Pr$_2$Ph	2,6-^{i}Pr$_2$Ph	1	THF	$(CH_2SiMe_3)_2$	L-LA	70	89	23.3	1.26	[107]

[a] The initiator is a lithium "ate" complex in which Li (as well as Y) is solvated by the donor ligand.
[b] The yttrium complexes was prepared but not tested.
[c] The complex is dinuclear with bridging H ligands.
[d] The complex is dinuclear with four terminal, and two bridging [RC(NR′)$_2$] ligands.
[e] ROP of β-butyrolactone furnished s-PHB with ca. 64% rr triads.

of poly(caprolactone) (PCL) of M_n = 42.6–103 K with PDI = 1.8–3.3) [98].

1.3.1. Ring opening polymerizations using transition metal amidinate complexes

By far the major application of [RC(NR′)$_2$] complexes, outside coordination polymerization, has been to ring-opening polymerization (ROP) of lactones, and D,L-lactide. These studies were motivated by the early work of Yasuda and co-workers on the use of lanthanocene complexes for controlled ROP of lactones [108]. One suspects, at least initially, that amidinates were also viewed as spectator ligands, analogous to π-Cp groups. However, the discovery that group 3 and lanthanide [RC(NR′)$_2$] complexes devoid of other nucleophilic ligands are also effective for ROP suggests a more active role. Indeed, amidines and especially cyclic guanidines are sufficiently nucleophilic that a metal is not even needed to effect ROP of lactones [109]. Listed in Table 5 are examples of transition metal amidinate complexes that have been studied in the context of ROP of ε-caprolactone (ε-CL) or D,L-lactide (D,L-LA). It should be noted that in many of these studies where yttrium complexes were reported, lanthanide analogs were investigated as well; the reader can refer to the original references for details of that work.



Many of these examples feature chain transfer and/or chain equilibration (through trans-esterification) at high conversion leading to a broad MWD and formation of lower MW polymer than expected. Some of the polymerizations are controlled, as is evident from the narrow MWD reported (entries 6, 14–16, 18–21) but in these cases, the complexes investigated generally suffer from low initiator efficiencies particularly at high [Mon]:[M] ratios, no doubt reflecting their moisture sensitivity. In the case of some bis-[RC(NR′)$_2$]Y alkoxide initiators (entries 14–16), formation of lower MW poly(lactic acid) (PLA) materials with narrow polydispersity was possible in the presence of an excess of iPrOH; evidently, equilibration between living (i.e. [RC(NR′)$_2$]$_2$Y-O-PLA) and dormant chains (i.e. H-O-PLA), via *reversible* reaction of the former with ^{i}PrOH was more rapid than propagation under the conditions studied. Generally speaking, neutral [RC(NR′)$_2$] complexes effect ROP of lactide (or β-butyrolactone) without epimerization of chiral material, though this has not always been systematically studied.

More recently, analogous studies have been reported for isoelectronic [R$_2$P(=O)NR′]– or [R$_2$P(=S)NR′]-Y complexes. Initially, *ansa*-[R$_2$P(=S)NR′]$_2$YN(SiMe$_3$)$_2$ [110] and *ansa*-[R$_2$P(=O)NR′]$_2$YN(SiMe$_3$)$_2$ [110b] were reported by Williams and co-workers (Chart 3). The latter complexes were dinuclear with bridging P=O moieties. Controlled polymerization of D,L-LA using the [R$_2$P(=S)NR′] complexes proceeded efficiently and in a quasi-living manner, while the dinuclear [R$_2$P(=O)NR′] initiators furnished PLA with double the MW expected. Evidently, the latter propagate as dinuclear complexes, but only one amido group per complex is viable for ROP of D,L-LA.

Further work from this same group revealed that the nature of the bridging group influenced the reactivity of these initiators (longer better than short) but had no effect on the tacticity of the PLA formed when using chiral diamines [111]. Kinetic studies showed that these dinuclear, amido complexes suffer from slow initiation, precluding the formation of PLA with a narrow MWD. When an alkoxide initiator was generated *in situ* controlled polymerization was observed (PDI = 1.15). In this case, it is interesting to note that two PLA chains per molecule of dinuclear Y initiator were formed.

Later work from this group showed, that in the solid state, this alkoxide complex was also dinuclear with P=O bridges, though a mononuclear amido initiator featuring coordinated THF could be prepared [112]. The latter complex effected heterotactic polymerization of D,L-LA while the dinuclear version afforded atactic PLA. Both of these were efficient initiators with complete conversion of monomer (0.5 M) within 10 min at room temperature at 2.5 mM initiator concentration.

Tris(amidate)yttrium complexes, which also adopt dinuclear structures in the absence of donor ligands, were reported by Schafer and co-workers [113]. Mono-nuclear THF adducts (Chart 3) were evaluated for controlled polymerization of ε-CL. Electron deficient complexes (Ar = p-CF$_3$-Ph, Ar′ = DIPP) were less reactive than electron rich materials (Ar = 2-naphthyl, Ar′ = DIPP) as would be expected for a nucleophilic, ring-opening process. The polymerizations are characterized by chain transfer or equilibration under the conditions studied as MW were largely independent of the ε-CL:Y ratio while PDI = 2.10–2.56.

1.3.2. Other polymerizations using transition metal amidinate complexes

As mentioned previously, transition metal [RC(NR′)$_2$] complexes have been employed in the polymerization of silanes. In the case of the [RC(NR′)$_2$]$_2$TiMe$_2$ or [RC(NR′)$_2$]$_2$ZrMe$_2$ complexes [6], the oligosilanes formed had reasonable degrees of polymerization ($X_n \sim 100$) upon activation with either MAO or B(C$_6$F$_5$)$_3$. This process, which involves a σ-bond metathesis mechanism (Scheme 9) in the case of metallocene catalysts [114] leads to branched, insoluble materials, at least when using 1° silanes, and since the process is step-growth, requires very high conversion of 2° silane to achieve significant degrees of polymerization. A late metal (APy)$_2$Pd complex reported by Kempe and co-workers [75] was much more active than Rh(I), Pd(II) or Pt(0) complexes tested for this purpose, and in the case of (MeSiH$_2$)$_2$ afforded soluble material. Since MeSiH$_3$ was the principal by-product formed, the process was thought to involve a L$_2$Pd = SiR$_2$ intermediate (Scheme 10), formed by α-elimination following oxidative addition of the disilane to Pd(0) [115]. The fate of the APy ligands in the Pd(II) precursor was not discussed.

A dinuclear Ru complex with a bridging amidinate ligand [(Cp*Ru)$_2$(μ-MeC(N^{i}Pr)$_2$)][PF$_6$] was used as a redox catalyst for atom transfer radical polymerization of methyl methacrylate and related monomers [73]. When generated *in situ* from the halide salt and NaPF$_6$, there was a lack of control, but by using pre-formed complex, PMMA with a narrow MWD was produced. An application to the synthesis of THF-MMA diblock copolymer was reported using an α-bromoisobutyrate macroinitiator derived from ROP of THF.

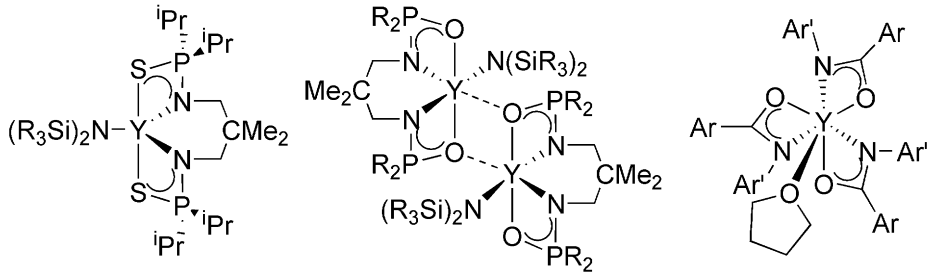
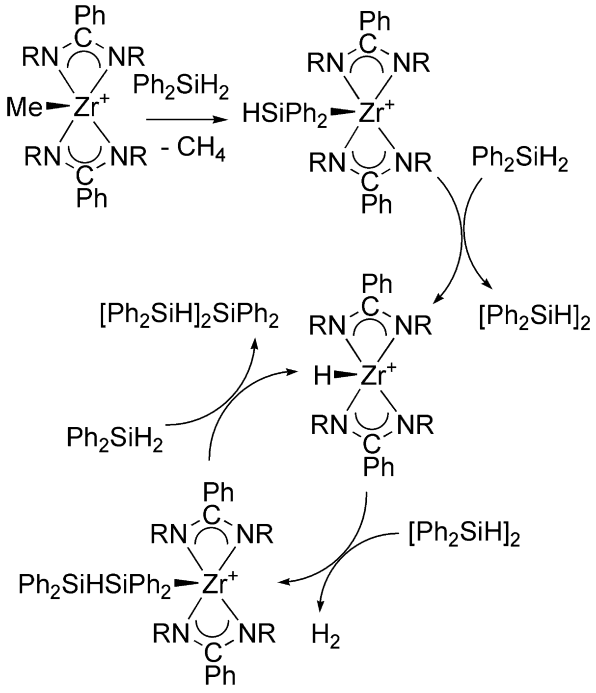
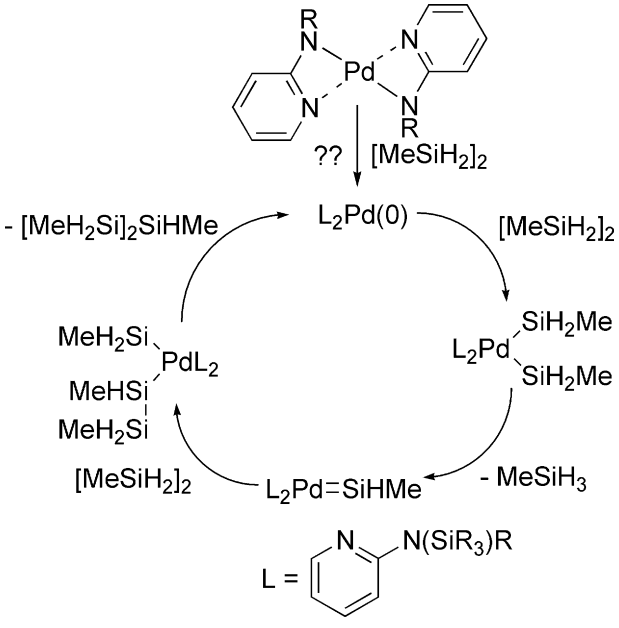


Chart 3.



Scheme 9.



Scheme 10.

There have been two studies on the use of early transition metal complexes for polymerization of methyl methacrylate or related monomers, likely motivated by the pioneering work of Yasuda and Collins employing lanthanocene, and group 4 metallocene initiators, respectively [116]. In a German patent, Erker and co-workers employed a titanocene bis(κ^1-O amidate) complex as an initiator for methyl vinyl ketone polymerization, using $B(C_6F_5)_3$ as an activator [117]. Presumably, a cationic amidate complex initiates polymerization. Hill and co-workers prepared a chelating bis-[$R_2P(NR')_2$] ligand from *trans*-1,2-diaminocyclohexane, Ph_2PCl and mesityl azide [118]. This ligand formed mononuclear, monodisilylamido Y complexes on reaction with $Y(N(SiR_3)_2)_3$. These chiral complexes were effective for the isotactic polymerization of MMA (*mm* = 70–88%) with a narrow MWD. As in the dinuclear lanthanocene complexes reported by Yasuda, very low initiator efficiencies (happily) conspired to produce very high MW polymer (M_w = 678–1240 K) in a living manner (PDI = 1.05–1.34).

As mentioned previously a Cu(II) bis-amidinate complex could be activated for ethylene polymerization using excess MAO [84]. This same formulation (i.e. MAO is needed in all cases) is also active for MMA polymerization and ROP of epoxides and lactones. It seems quite unlikely that the same Cu complex can be involved in these diverse polymerization processes. More details on the polymerization of MMA were provided in a subsequent paper [119]. Treatment of the Cu(II) complex with MAO (or TIBAL) results in immediate reduction to Cu(I); over-reduction with TIBAL results in precipitation of Cu(0). By analogy to the nucleophilic, addition polymerization of carbodiimides, it seems reasonable that a Cu(I) [$RC(NR')_2$] complex, formed *in situ,* could be effective for "anionic" addition polymerization of MMA or ROP of epoxides and lactones, particularly if these are activated for nucleophilic attack by MAO. Experiments with $Al(OiPr)_3$ were inconclusive, presumably this compound is ineffective for reducing Cu(II). In the paper, only traces of polystyrene were produced using these formulations [120], suggesting a radical mechanism arising from homolysis of a Cu(II) alkyl is unlikely.

1.4. Concluding remarks

It is evident from the foregoing that transition metal amidinate and related complexes exhibit a rich chemistry with important applications to polymerization catalysis and polymer synthesis. By far the largest application has been to coordination polymerization; unlike their metallocene "analogs" the early metal complexes have applications to living olefin polymerization, while their activation chemistry is often complicated by ligand abstraction or modification in the presence of alkylaluminum compounds, including the ubiquitous MAO. Useful and important applications to stereoregular diene polymerization have emerged using group 3 [$RC(NR')_2$] complexes. These compounds are also very useful in controlled ROP of lactones and lactide to furnish compostable thermoplastics. The field of late metal mediated polymerization using [$RC(NR')_2$] complexes is still in its infancy; it is uncertain whether these electron

rich, hemi-labile complexes will have important applications to coordination polymerization – their nucleophilic character suggest considerable potential for anionic polymerization of susceptible monomers. We can look forward to continued interest and research activity in these and allied areas; particularly the development of configurationally stable, chiral, mono- or bis-amidinate complexes holds promise for stereocontrolled polymerization above and beyond that currently achievable.

Acknowledgements

The author would like to thank the Natural Science and Engineering Research Council of Canada, Nova Chemicals Corporation of Calgary, Alberta, Canada, and The University of Akron for generous financial support of his work cited in this review. The author would also like to thank The University of Akron for access to the scientific literature in connection with preparing this manuscript.

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