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Niobium complexes as catalytic precursors for the polymerization of olefins

Anna Maria Raspolli Galletti*, Guido Pampaloni

Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, I-56126 Pisa, Italy

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Dedicated to Professor Fausto Calderazzo on the occasion of his 80th birthday, with our best wishes and gratitude for his teaching.

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ABSTRACT

Until now niobium compounds have been very rarely applied for the polymerization of olefins, notwithstanding their moderate cost, limited toxicity and the large availability of stable oxidation states, which makes them versatile precursors. The data reported to date on ethylene and norbornene polymerization catalysts are discussed, with particular reference to the evolution of the approach to the design of these systems, starting from isoelectronic, isolobal or isostructural relationships with Group 4 metallocene catalysts. The catalytic performances in ethylene and norbornene polymerization of the niobium precursors with cyclopentadienyl, diene, amido, amidinate, pyrazolylborate ligands have been compared. The most recent results have been discussed, comparing the reported activities for complexes with phenolate, bis(imino)pyridine and N,N-dialkylcarbamate ligands.

Significant improvements in norbornene ROMP have been recently achieved, whilst for ethylene polymerization the process of optimization of the niobium-based catalytic systems still needs hard work.

1. Introduction

The observations that Ziegler and coworkers (ethylene polymerization at ambient temperature and pressure) [1] and Natta and coworkers (preparation of stereospecific polymers from α-olefins) [2] reported in 1955 represented the starting point of a new era in polymer science and industry. Since then, we have witnessed the evolution of a new generation of catalysts and polyolefin materials which originate from studies on homogeneous, metallocene- and non-metallocene-based polymerization precursors [3]. Group 4 metallocenes and half-sandwich metal–amide complexes have been at the forefront of these developments, followed in the first half of the 1990s, by a crescent interest for “non-metallocene” systems based on transition metals different from titanium, zirconium and hafnium, such as nickel [4] or and iron [5].

Homogeneous systems based on Group 5 metals have been much less studied than the Group 4 congeners. The initial approach to the design of the catalytic precursors involving vanadium, niobium and tantalum was to exploit relationships between the monoanionic Cp ligand and isolobal dianionic fragments. Substitution of one Cp ligand from a Group 4 metallocene for an isolobal dianionic ligand and replacement of the metal by one from Group 5 gives access to high-valent 14-electron cationic alkyl species that was expected to have metallocene-like reactivity. Complexes supported by a variety of such dianionic ligands have been investigated, although activities are generally lower compared to their Group 4 analogues.

Within Group 5 metals, much attention has been devoted to vanadium derivatives which have been largely employed as olefins polymerization catalyst also in industrial processes [3b,6], the heavier congeners (niobium and tantalum) having received considerably less attention [3b,7]. Although the wide availability of stable oxidation states for niobium and tantalum, allows one to widen the study of the influence of the charge on the polymerization steps, ten years ago Kempe stated that *niobium and tantalum compounds live in the shadow of metal complexes of Group 4* [8].

In view of the generally observed increase of the M–L bond energy on going down a group of transition metals, tantalum complexes are generally less reactive than the niobium ones [9]. A recent paper by Wolczanski and coworkers [10] has shown that large differences in the kinetics of the olefin substitution reactions are observed for compounds of general formula $M(OSi^tBu_3)$(olefin), the niobium derivative dissociating the olefin much faster than the tantalum analogue. For this reason niobium derivatives will be treated preferentially in this review which is mainly devoted to the catalytic application of the metal complexes. We limit our main discussion to niobium derivatives, that appear particularly intriguing due to the low cost of the metal, limited toxicity and their lower sensitivity to deactivation by polar species with respect to the oxophilic derivatives of Group 4 metals. This last aspect appears particularly important in the perspective of the direct metal-

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* Corresponding author. Tel.: +39 050 2219226; fax: +39 050 221960.
E-mail address: roxy@dcci.unipi.it (A.M. Raspolli Galletti).

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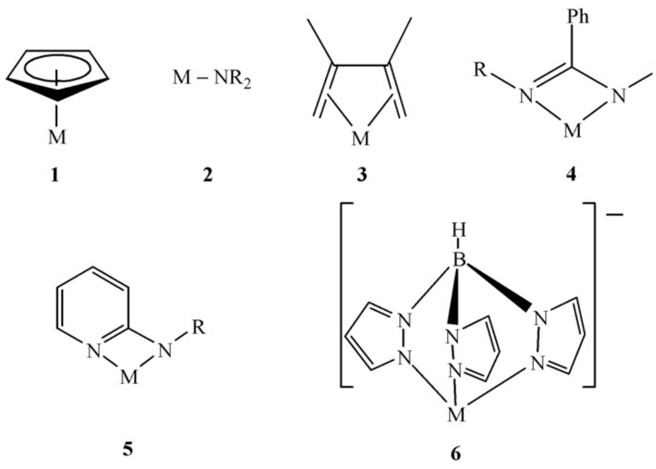


Scheme 1. Types of M–L fragments used in the catalytic precursors.

mediated copolymerization of olefins with polar monomers, one of the most pursued goals in the field of polymerization catalysis [11].

Several attempts to develop active niobium catalysts for olefin polymerization reactions refer to the isoelectronic, isolobal or isostructural relationships with Group 4 metal complexes. Derivatives based on cyclopentadienyl, **1**, amido, **2**, diene, **3**, and amidinate, **4** ligands, see Scheme 1, have been explored. The low-to-moderate performances observed with this approach prompted to investigate a larger range of precursors. Other niobium precursors which have been recently employed as catalysts for olefins polymerization contain aminopyridines, **5**, and tris-pyrazolylborates, **6**, see Scheme 1. Ethylene and norbornene have been the mostly investigated monomers and only a limited number of studies have been reported on the activation of styrene, 1-butene and methyl metacrylate. For this reason, this review will deal mostly with ethylene and norbornene activation.

In this review the performances of the catalytic precursors will be classified according to the employed monomer. In order to present homogenous data, the catalyst's activity will be given in $g_{polymer}\ mmol^{-1}\ bar^{-1}\ h^{-1}$ for ethylene and in $g_{polymer}\ mmol^{-1}\ h^{-1}$ for liquid monomers. Although overestimated performances can be obtained for very short polymerization times, the catalytic activity will be classified as high (1000–100), moderate (100–10), low (10–1) and very low (<1), according to Gibson's suggestion [12].

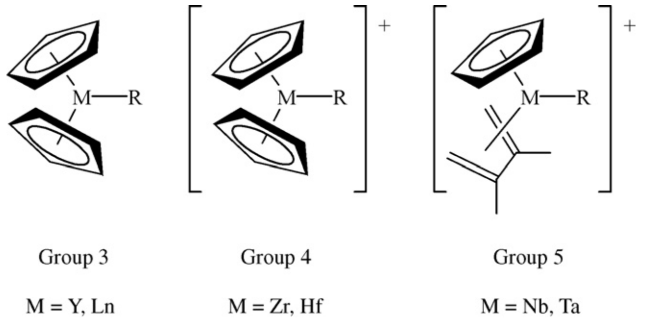
2. Niobium catalysts for ethylene polymerization

2.1. Complexes containing cyclopentadienyl fragments

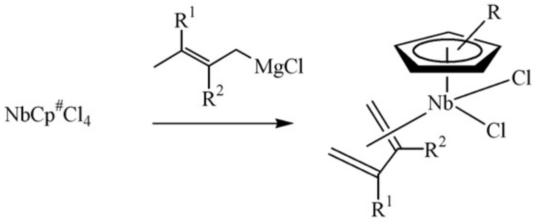
Many papers have been published about the catalytic activity of systems comprising bis-cyclopentadienyl metal complexes and methylaluminoxane (MAO). The high activity of the Group 4 metallocenes justified additional research within different systems such as the niobium(IV) bis-cyclopentadienyl derivative $NbCp_2Cl_2$. These studies unequivocally confirmed that such species are characterised by a low activity for the polymerization of ethylene at atmospheric or superatmospheric pressure even operating with MAO/Nb molar ratios as high as 4000 [13]. The immobilization of $NbCp_2Cl_2$ on MAO-modified silica did not improve the activity in ethylene polymerization [13c]. The low activity of these species was considered a consequence of the inaccessibility of the cation species $[MCp_2R]^+$ under the reaction conditions used for the polymerization runs.

2.1.1. Half-sandwich diene complexes

In order to develop an ethylene polymerization catalyst based on niobium, Mashima and coworkers [14] based on an approach inspired by the observation that the fragments of MCp(η^4-1,3-diene) (M = Nb, Ta) are isoelectronic and isolobal to "MCp_2", M = Zr, Hf. Isoelectronic cyclopentadienyl species of Groups 3, 4 and 5 metals are reported in Scheme 2.



Scheme 2. Isoelectronic bis(cyclopentadienyl)alkyl species of Groups 3, 4 and 5.



$Cp^\# = \eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_5Me_5$
R = Me, $R^1 = R^2$ = H; **7a**
R = Me, R^1 = Me, R^2 = H; **7b**
R = Me, $R^1 = R^2$ = Me; **7c**
R = H, $R^1 = R^2$ = Me, **8**

Scheme 3. Preparation of Nb(RCp)(η^4-diene) derivatives.

In consideration of these relationships, the niobium precursors were prepared by reaction of $NbCpCl_4$ and allylMgCl according to Scheme 3 and tested in ethylene activation [15–17]. The catalytic activities of these monodiene complexes in the presence of methylaluminoxane as co-catalyst are reported in Table 1.

The addition of MAO is necessary for the activation of the precursors to form the catalytically active species. The authors propose that MAO acts both as alkylating reagent and ligand exchange partner between aluminium and niobium, thus forming a cationic species. The catalytic activity, which is always moderate, depends on steric and electronic effects of the two different ligands,

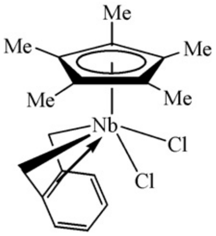
Table 1
Polymerization of ethylene catalyzed by the niobium–diene complexes **7–8** /MAO and niobium-o-xylylene **9**/MAO complexes[a].

Entry	Nb precursor	T (°C)	A[b]	$M_n \times 10^{-4}$	M_w/M_n	Ref.
1	**7a**	20	38.7	8.29	1.30	[15,16]
2	**7a**	0	14.50	4.95	1.07	[15,16]
3	**7a**	−20	10.65	2.36	1.05	[15,16]
4	**7b**	20	19.22	3.95	1.16	[15,16]
5	**7b**	0	6.94	2.22	1.07	[15,16]
6	**7b**	−20	1.02	0.51	1.09	[15,16]
7	**7c**	20	35.23	10.54	1.18	[15,16]
8	**7c**	0	21.87	8.16	1.08	[15,16]
9	**7c**	−20	12.71	4.10	1.05	[15,16]
10[c]	**8**	20	6.89	n.d.	n.d.	[16]
11[d]	**8**	0	13.03	4.88	4.39	[17]
12	**9**	20	43.7	3.10	1.65	[19]

[a] Reaction conditions: solvent, toluene; time, 1 h; Al/Nb, 500 mol/mol.
[b] Activity: $g_{polymer}(\text{mmol Nb})^{-1}\ bar^{-1}\ h^{-1}$.
[c] Reaction time: 3 h.
[d] Reaction time: 2 h.

i.e. cyclopentadienyl and diene. These species showed a marked decrease of the activity when the temperature was increased above 20 °C. In agreement with the lower stability of compounds containing C_5H_5 rings derivatives with respect to the permethylated ones [18], **8** resulted less stable and, consequently, the resulting polymer was characterized by a broad polydispersity. In contrast, for the more thermally stable complexes **7** a narrow polydispersity of the produced polyethylene was always obtained (M_w/M_n: 1.05–1.30), thus suggesting the character of living polymerization.

As an alternative to these η^4-diene complexes, Mashima reported also the catalytic activity of the η^4-o-xylylene complex **9** [19]. The o-xylylene ligand can coordinate to the niobium center in a η^4 fashion analogous to η^4-1,3-diene ligands. This precursor, in the presence of an excess of MAO, was found to be more active than the corresponding niobium butadiene system **7a** to give a polyethylene having a relatively narrow polydispersity (compare entry 12 with entry 1, Table 1). This result suggests that the performances of these niobium monocyclopentadienyl complexes can be tuned by the proper selection of the diene-type ligand. Analogously to that which was found for butadiene complexes **7**–**8**, the catalytic system **9**/MAO was also more active than the corresponding tantalum complex.



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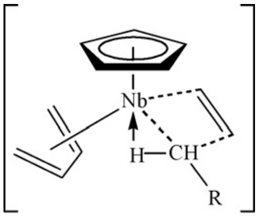
The catalytic system **7**/MAO was also studied using density functional theory (DFT) [20]. This study demonstrates that the active species, assumed to be of type [NbCp(η^4-1,3-butadiene)R]$^+$, **10**, significantly differs from the isoelectronic species [ZrCp$_2$R]$^+$ because of the weakness of the interaction between the incoming ethylene and the methyl cation **10**. As a matter of fact, no free energy minimum was found. The ethylene insertion into the metal–alkyl bond has an energy barrier of 4 kcal/mol for **10**, R = CH_3, and 6 kcal/mol for **10**, R = C_2H_5. This fact has been attributed to the absence of an agostic interaction sketched in **11**, which is known to stabilize the ethylene transition states in the case of the isoelectronic neutral Group 3 or cationic Group 4 systems [21].



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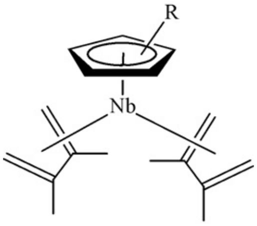
As a consequence, due to the absence of strong agostic interaction, different conformations easily interconvert and the most important free energy barriers result 19 kcal/mol for propagation, 32 kcal/mol for termination via β-hydrogen transfer to a coordinated ethylene molecule, and 40 kcal/mol for the alternative termination process via β-hydrogen elimination. According to the authors, at the moment, any possible termination mechanism, including also a via alkylidene pathway, can be operative and the nature of substituents, solvent, counterion will decide its reliability. The high propagation barrier may be compensated by the good availability of a free coordination site for the incoming monomer due to the weak π-type complexation ability and also to the small solvent coordination on the active site.

Table 2
Polymerization of ethylene catalyzed by the niobium bis-diene complexes **12**–**13**/MAO[a].

Entry	Nb precursor	T (°C)	A[b]	$M_n \times 10^{-4}$	M_w/M_n	Ref.
13	**12**	20	9.03	16.86	2.24	[16]
14	**12**	0	17.03	31.80	2.94	[16]
15	**12**	−20	7.55	27.14	4.13	[16]
16	**13**	20	24.65	3.07	1.18	[15,16]
17	**13**	0	21.95	2.82	1.13	[15,16]
18	**13**	−20	12.48	1.42	1.06	[15,16]

[a] Reaction conditions: solvent, toluene; time, 1 h; Al/Nb, 500 mol/mol.
[b] Activity: $g_{polymer}(mmol\ Nb)^{-1}\ bar^{-1}\ h^{-1}$.

The study on niobium–diene complexes was extended to bis-diene complexes **12** and **13** prepared by reaction of NbCl$_4$(η^5-C_5R_5) with two equivalents of Mg(2,3-dimethylbuta-1,3-diene) in THF [15,22]. These compounds to exist in two forms with the diene moiety coordinated either *supine* or *prone* to niobium. The diene coordinated in the *supine* fashion has a more pronounced σ-character than the *prone* one [15]. As a matter of fact, when compounds **12** and **13** are treated with MAO, they undergo selective ligand exchange at the *prone* diene ligand with the methyl group of MAO to generate a 14-electron catalytically active species similar to that obtained from the monodiene complexes and MAO [15]. No activation is required when **12** or **13** were treated with B(C_6F_5)$_3$ or with Et$_3$Al [15]. The catalytic performances of **12** and **13** precursors activated by MAO are reported in Table 2.



R = H, **12**; Me, **13**

The similarity of the catalytic activities between the mono- and the bis-diene derivatives, suggests that similar active species are generated under the same experimental conditions. Moreover, the permethylated derivative **13** showed higher catalytic activities and narrower polydispersities with respect to **12** (entries 16–18 vs. entries 13–15, Table 2) in view of the higher stability of the former and, as in the case of the monodiene derivatives (vide supra), the niobium precursors showed a better catalytic activity than the corresponding tantalum derivatives [15].

An interesting paper by Mashima and coworkers appeared some years ago [23] showing how elements so close in the Periodic Table, as niobium and tantalum, afford complexes of the same composition but characterized by a large difference as far as the thermal stability is concerned. As a matter of fact, NbCp*Me$_2$(η^4-butadiene) is thermally unstable and affords a species which is a catalyst for the ring opening metathesis polymerization (ROMP) of norbornene (vide infra), whilst the tantalum analogue is a thermally stable compound and a promoter of the living ethylene polymerization reaction [15–17].

2.1.2. *Half-sandwich imido derivatives*

In view of the isolobal relationship between the dianionic imido ligand, **2**, a strong π donor ligand with a marked ability to stabilize high-valent metal complexes [24], and the cyclopentadienide anion [25], numerous papers have been published since the early 1990s suggesting that half-sandwich imido complexes of the Group

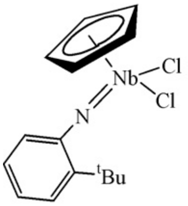
Table 3
Polymerization of ethylene catalyzed by complexes **14**–**18**.

Entry	Nb precursor	Activator (mol/Nb)	T (°C)	A[a]	$M_n \times 10^{-4}$	M_w/M_n	Ref.
19[b]	**14**	Et_2AlCl (30)	25	0.6	n.d.	n.d.	[26c]
20[c]	**15**	$[PhNMe_2H][B(C_6F_5)_4]$ (1)	50	Traces	–	–	[26c]
21[d]	**16**	MAO (2448)	25	0.9	n.d.	n.d.	[31]
22[d]	**17**	MAO (2448)	25	1.7	n.d.	n.d.	[31]
23[d]	**18**	MAO (2448)	25	1.8	n.d.	n.d.	[31]

[a] Activity: $g_{polymer}(mmol\,Nb)^{-1}\,bar^{-1}\,h^{-1}$.
[b] Reaction conditions: solvent, toluene; time, 1 h; $P_{ethylene}$, 1 bar.
[c] Reaction conditions: solvent CH_2Cl_2/isobutane; time, 1 h; $P_{ethylene}$, 10 bar.
[d] Reaction conditions: solvent, toluene; time, 2 h; $P_{ethylene}$, 2 bar.

5 metals of general formula $MCp(NR)X_2$ could behave similarly to the Group 4 metallocenes as far as the olefin polymerization reaction was concerned [26].

Gibson studied in detail the catalytic activity of niobium imido precursors **14**–**15** for ethylene polymerization in the presence of aluminium or boron co-catalysts [26c]. As reported in Table 3, the activity observed for the dichloride procatalyst **14** activated by Et_2AlCl was very low. In attempt to stabilize alkyl intermediates, the pentamethylcyclopentadienyl dimethyl derivative **15** was prepared and tested using $[PhNMe_2H][B(C_6F_5)_4]$ as co-catalyst. Notwithstanding this modification, the productivity of **15** was also negligible [26c].



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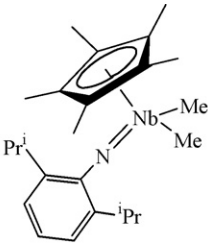

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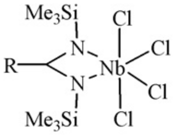
As a consequence of these preliminary unsuccessful results, this type of catalyst was abandoned. The observed inactivity *is not understood* [27] but it has been related to the difficulty of generating half-sandwich alkyl cations from the dialkyl precursors due to the inefficacy of the alkyl abstraction activators [27] or to the propensity of these imido species for bridging to form inactive dinuclear complexes [28].

2.2. Non-metallocene derivatives (benzamidinato, amido, aminopyridine, pyrazolylborate, bis(imino)pyridines)

The low activity generally observed with the niobium half-sandwich compounds described in the previous sections, has stimulated research into non-metallocene compounds containing ligands with properties similar to the cyclopentadienyl group. The benzamidinato ligands, **4**, $PhC(NR)_2$, R = alkyl, silyl; Ph = aryl or substituted aryl ring, are hard four-electron donors with steric requirements intermediate between those of the cyclopentadienyl- and the pentamethylcyclopentadienyl ligands [29]. Interestingly, the presence of the phenyl ring allows tailoring properties such as bite- or cone angles by variation of the substituents on the aromatic ring [30].

In order to prevent the formation of bis-benzamidinato complexes (commonly formed when unsubstituted aryl benzamidinato ligands are present) bulky 2,4,6-tri-isopropyl substituents on the aryl rings of the benzamidinato ligands were used for the preparation of the niobium benzamidinato precursors **16**–**18**, which were tested in ethylene polymerization using MAO as co-catalyst [31]. The catalytic performances, reported in Table 3 (entries 21–23), demonstrate a generalized low activity of these species: further studies were consequently discontinued [31].



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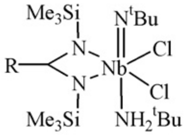

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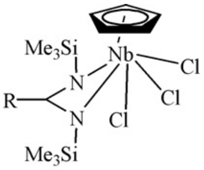

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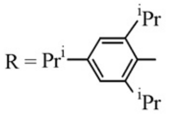
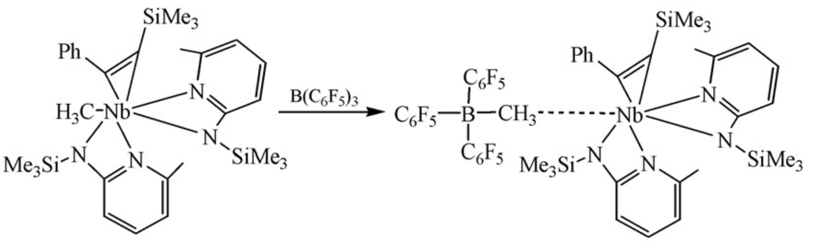


Another type of ligands studied for the access to active niobium polymerization catalysts is represented by amido groups. These ligands offer interesting alternatives to Cp ligands as stabilizing components of cationic early transition metal complexes [32,33]. The Nb(V) precursor with diamido ligands **19**, characterized by the presence of a rigid diamide ligand with C_2 symmetry, was synthetized and tested in polymerization reactions [34]. This compound, in the presence of MAO as co-catalyst, resulted completely inactive in the ethylene polymerization. On the other hand, as it appears from the data of Table 4 (entries 24–26), compound **19**

Table 4
Activity of niobium complexes **19**, **21**, **24**–**26** in the polymerization of ethylene and styrene.

Entry	Nb precursor	Monomer	Activator (mol/Nb)	Time (min)	A[a]	$M_n \times 10^{-4}$	M_w/M_n	Ref.
24[b]	**19**	Ethylene	MAO (1000)	60	–	n.d.	n.d.	[34]
25[c]	**19**	Styrene	MAO (1000)	60	0.64	2.1	1.91	[34]
26[c]	**19**	Styrene	MAO (1000)	180	0.7	1.3	2.9	[34]
27[d]	**21**	Ethylene	$^iBu_3Al$ (n.d.)	240	0.7	3.6	1.8	[8]
28[e]	**24**	Ethylene	$B(C_6F_5)_3$ (1)	5	100	n.d.	n.d.	[37]
29[e]	**25**	Ethylene	$B(C_6F_5)_3$ (1)	5	130	n.d.	n.d.	[37]
30[e]	**26**	Ethylene	$B(C_6F_5)_3$ (1)	5	20	n.d.	n.d.	[37]

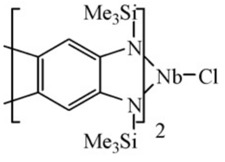
[a] Activity: $g_{polymer}(Nb)^{-1}\,bar^{-1}\,h^{-1}$ for ethylene and $g_{polymer}(mmol\,Nb)^{-1}\,h^{-1}$ for styrene.
[b] Reaction conditions: solvent, toluene; $P_{ethylene}$, 2.4 bar; T, 20 °C.
[c] Reaction conditions: solvent, toluene; T, 20 °C.
[d] Reaction conditions: solvent, toluene; $P_{ethylene}$, 6.5 bar; T, 80 °C.
[e] Reaction conditions: solvent, toluene; $P_{ethylene}$, 1 bar; T, 25 °C.



20 **21**

Scheme 4. Preparation of the aminopyridinato zwitterionic niobium complex **21** [8].

was able to polymerize styrene (MAO was used as co-catalyst): a living polymerization process was observed, to give a polystyrene with polydispersity typical of a single-site catalyst [34].



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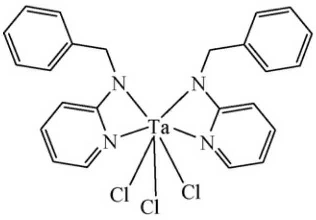
The low catalytic activities and the failure to displace the chloride ligand and get a cationic complex (reaction of **19** with $NaBPh_4$), were related to the steric hindrance of the $SiMe_3$ groups which, according to the authors, precluded *easy access to the metal center* [34].

The preparation of amido niobium complexes containing a η^2-bound substituted alkyne was reported by Kempe and coworkers, who obtained the aminopyridinato zwitterionic compound, **21**, by reaction of **20** with $B(C_6F_5)_3$ [8], see Scheme 4.

At variance with the tantalum derivatives **22** and **23**, which, once activated with MAO, resulted in efficient ethylene polymerization systems with activities as high as ca. 5000 $g_{polymer}$ $mmol^{-1}$ bar^{-1} h^{-1} [35], compound **21** polymerizes ethylene without the addition of a co-catalyst, but it rapidly decomposes at 80 °C, thus showing a quite low activity (entry 27, Table 4).



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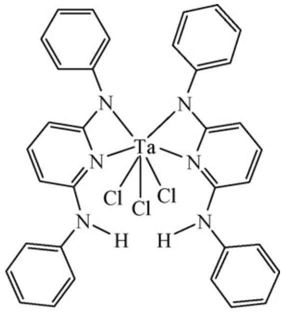
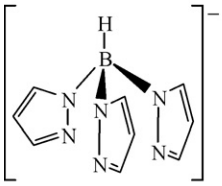


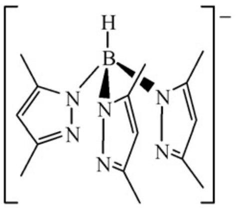
23

The extent of the decomposition was reduced by addition of $^{i}Bu_3Al$ as scavenger but the observed activity was still low. This result was related to the thermal instability of these systems which do not survive at the temperature conditions necessary for the polymerization reaction. Species **21**, when activated with MAO, selectively (98%) dimerizes 1-butene to 2-ethylhexene [8].

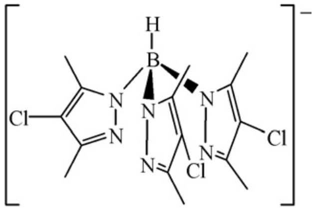
The isolobal relationship between imido and η^2-bound alkyne ligands as well as between Cp and Tp′ ligands [Tp′ = substituted hydridotris(pyrazolyl)borate] [36] has also been used in the design of the $NbTp^{Me2}Me_2(PhC\equiv CMe)$, **24**, $NbTp^{Me2,4\text{-}Cl}Me_2(PhC\equiv CMe)$, **25**, and $[NbTpMe_2(PhC\equiv CMe)]$, **26**, derivatives [37]. The dimethyl complexes show an appreciable activity in ethylene polymerization carried out in toluene solution in the presence of methyl abstracting agent such as $B(C_6F_5)_3$ (entries 28–30, Table 4). The catalytic activity strongly depends on the nature of the hydridotris(pyrazolyl)borate ligand: bulky Tp′ ligands cause a much higher activity with respect to the unsubstituted Tp (compare runs 28 and 29 with run 30, Table 4). The positive effect of sterically demanding ligands has been related [37] to the steric shielding of the metal center, thus preventing the active species decomposition via association to give inactive dinuclear species.



Tp



Tp^{Me2}



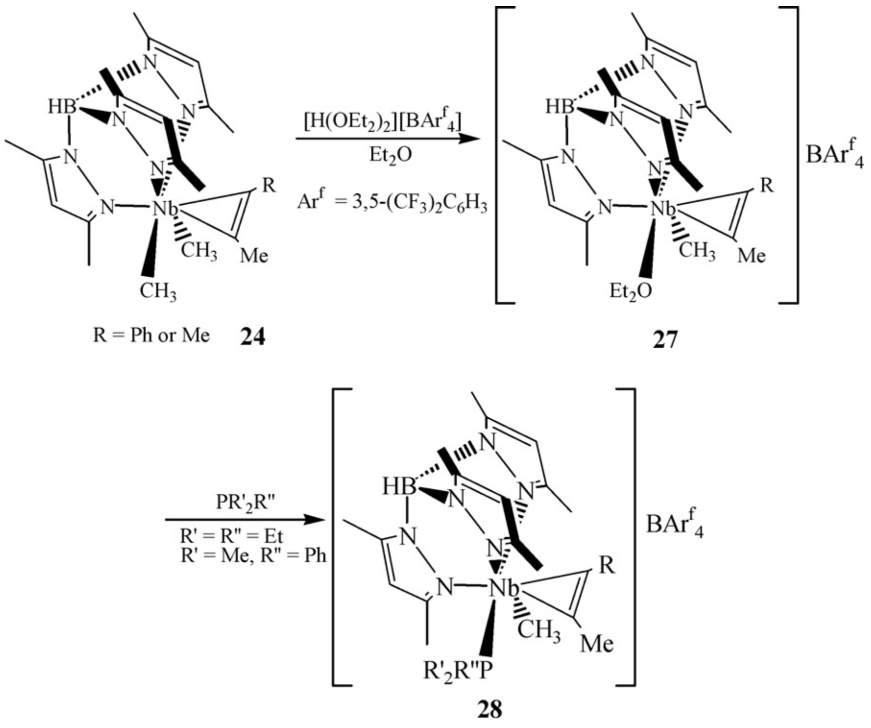
$Tp^{Me2,4\text{-}Cl}$

The dimethyl compound **24** reacts with the Brookhart cation $[H(OEt_2)_2[BArf_4]]$, Arf = 3,5-$C_6H_3(CF_3)_2$ [38] to give the diethylether-stabilized methyl cation **27** (structurally characterized), a rare example of alkyl cation of niobium directly related to the active species in ethylene polymerization, Scheme 5. Compound **27** can be further stabilized by reaction with a tertiary phosphine to give **28** [39].

2.3. Complexes with phenolate ligands

As noted in the preceding section, the niobium precursors designed on the basis of isolobal analogies with the Group 4 metallocene derivatives, did not give appreciable results as far as the activity that these compounds showed in the polymerization reactions of ethylene.

In the search of other ligands able to give complexes of Group 5 metals to be used as promoters for α-olefin polymerization, particular attention was devoted to chelating aryloxide ligands [40] in view of the high activity shown by vanadyl complexes bearing bi- or triphenolate chelate ligands [41] in the presence of Me_2AlCl and ethyl trichloroacetate (ETA) as re-activator [42].



Scheme 5. Synthesis of methyl tris(pyrazolyl)borate cations of Nb(III) [39].

Table 5
Polymerization of ethylene catalyzed by the niobium complexes **29**–**33** and **35**–**39**[a] [43,49].

Entry	Nb precursor	Co-catalyst	Re-activator	A^b	$M_n \times 10^{-4}$	M_w/M_n
31	**29**	Et_2AlCl	ETA	41	6.3	2.0
32	**30**	Et_2AlCl	ETA	14	6.3	2.1
33	**31**	Et_2AlCl	ETA	45	7.1	2.5
34	**32**	Et_2AlCl	ETA	90	6.7	2.5
35	**32**	Et_2AlCl	–	6	24.6	15
36	**32**	Me_2AlCl	ETA	20	56.9	2.0
37	**32**	Me_2AlCl	–	4	20.5	20
38	**32**	MAO	ETA	1	n.d.	n.d.
39	**33**	Et_2AlCl	ETA	87	6.9	2.4
40	**35**	Me_2AlCl	ETA	20	31.9	2.4
41	**36**	Me_2AlCl	ETA	19	32.4	2.2
42	**37**	Me_2AlCl	ETA	84	29.6	2.5
43	**38**	Me_2AlCl	ETA	9	39.1	2.3
44	**39**	Me_2AlCl	ETA	20	43.6	2.4

[a] Reaction conditions: precursor, 5 μmol; solvent, toluene; time, 1 h; Al/Nb, 800 mol/mol; ETA, 0.1 ml; $P_{ethylene}$, 1 bar; T, 50 °C.

[b] Activity: $g_{polymer}(mmol\ Nb)^{-1}\ bar^{-1}\ h^{-1}$.

Table 6
Polymerization of ethylene catalyzed by the niobium precursors **41**–**44**/MMAO[a] [55].

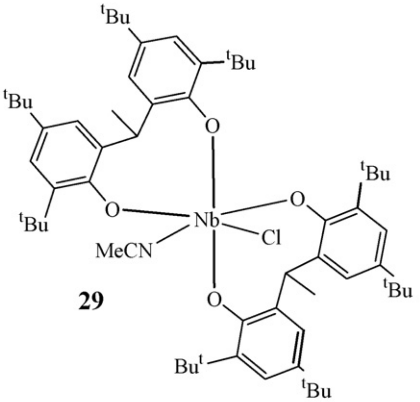
Entry	Nb precursor	Al/Nb mol/mol	A^b	$M_n \times 10^{-4}$	M_w/M_n	$T_m{}^c$ (°C)
45	**41**	100	15	4.25	11.3	140.3
46	**42**	500	70	0.33	4.3	133.2
47	**43**	500	15	n.d.	n.d.	129.8
48	**43**	500	22	n.d.	n.d.	127.4
49	**44**	500	11	n.d.	n.d.	128.2

[a] Reaction conditions: solvent, toluene; time, 10 min; $P_{ethylene}$, 1 bar.

[b] Activity: $g_{polymer}(mmol\ Nb)^{-1}\ bar^{-1}\ h^{-1}$.

[c] Determined by DSC.

In an attempt to understand the coordinating characteristics of these chelating aryloxides and to investigate the potential catalytic capabilities of early transition metal centres different from vanadium, Redshaw and coworkers extended the investigations to high-valent niobium [43], which is known to exhibit a rich aryloxide chemistry [44]. The new mono- and dinuclear niobium(V) complexes **29**–**33** incorporating linked aryloxide ligands were prepared, characterized and tested in ethylene polymerization in the presence of an organoaluminium co-catalyst [43].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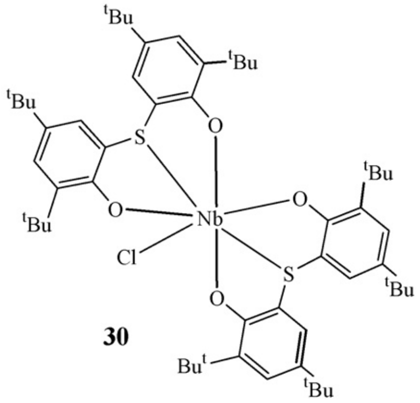
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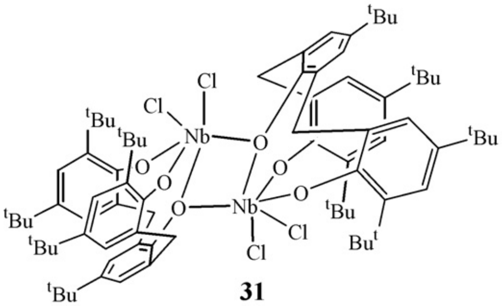
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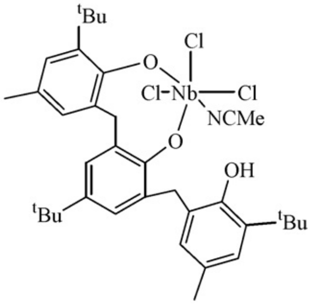
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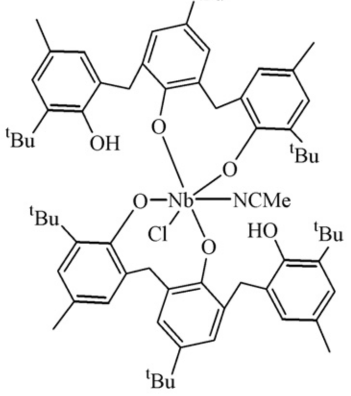
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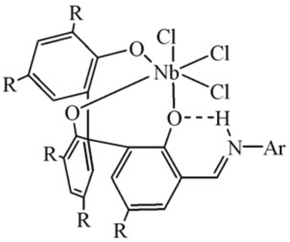
The catalytic performances observed in the presence of different organoaluminium co-catalysts are reported in Table 5. The nature of the co-catalyst is crucial: for example, no catalytic activity was observed in absence of aluminium co-catalyst, and was only little increased in the presence of MAO (entry 38, Table 5). On the contrary, the use of Me_2AlCl or (better) Et_2AlCl, in the presence of ethyl trichloroacetate as re-activator, allowed one to reach activities up to 90 $g_{polymer}(mmol\ Nb)^{-1}\ bar^{-1}\ h^{-1}$ (entries 34 and 39, Table 5). In the absence of ethyl trichloroacetate the catalytic activity largely decreases (compare entry 34 with entry 35, Table 5).

A niobium complex bearing a C-capped tris(phenolate) ligand with a pendant imine arm (**34**) was tested, but it was inactive in ethylene polymerization in the presence of a number of aluminium co-catalysts [45].

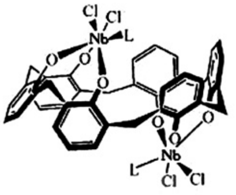


Ar = 2,6-diisopropylphenyl
R = *tert*-butyl

34

Redshaw and coworkers extended their research studying the catalytic behaviour of a very particular class of chelating aryloxide ligands: methylene- and dimethyleneoxa-bridged calix[*n*]arene [46]. Although catalytic activities reported are at best moderate, the only exception being a chromium(III)calix[4]arene system [47], these macrocyclic ligands have recently attracted increasing interest in view of the high activity shown by vanadyl precursors bearing dimethyleneoxa-bridged ($-CH_2OCH_2-$) oxacalix[3]arene [48].

The use of this class of calixarene ligands was extended to niobium and tantalum and the corresponding complexes were isolated and fully characterized. The niobium complexes were tested in ethylene polymerization [49]. No polymerization was observed in the absence of aluminium co-catalysts for both niobium and tantalum derivatives. When activated with either MAO, Me_3Al, Me_2AlCl or Et_2AlCl, either with or without ethyl trichloroacetate as re-activator, niobium(V) calixarene derivatives **35**–**39** showed a poor-to-moderate activity for the polymerization of ethylene, the highest activity [84 $g_{polymer}(mmol\ Nb)^{-1}\ bar^{-1}\ h^{-1}$] being reached employing the ($-CH_2OCH_2-$)-bridged precursor **37** (entry 42, Table 5).



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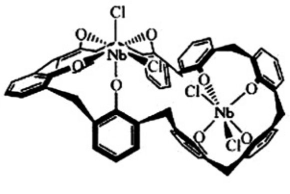

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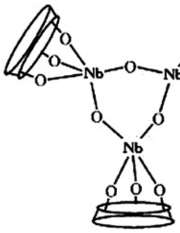

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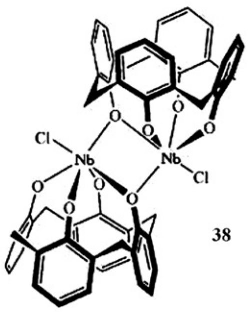

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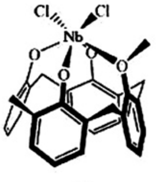
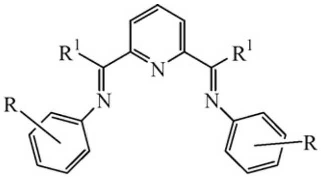


39

= *p-tert*-butylhexahomooxacalix[3]arene

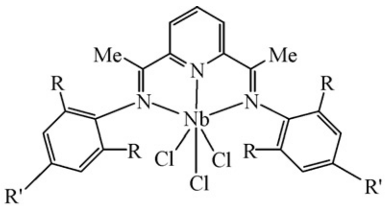
2.4. Complexes with bis(imino)pyridine ligands

In 1998–1999 Brookhart and coworkers [5b] and Gibson and coworkers [5a,50] reported that pentacoordinate iron(II) or cobalt(II) derivatives containing bis(arylimino)pyridine ligands, **40**, efficiently polymerize ethylene in the presence of methylalumoxane (MAO). Subsequent work showed that stereochemical and electronic factors influence the yield, the molecular weight and the microstructure of the polymer [51]. Further studies have been performed on several transition metals including noble metals [3b,52], vanadium [53] and Group 4 metals [54].



40

As far as the heavier homologues of Group 5 metals are concerned, Shiono and coworkers have recently reported the synthesis of niobium(III) complexes **41**–**44** containing the 2,6-bis{1-(arylimino)ethyl}pyridine ligand [55]. These precursors, characterized by different steric hindrance of the alkyl substituents on the N-aryl rings, were tested in ethylene polymerization carried out in the presence of ^{i}Bu-modified MAO (MMAO) [55]: the catalytic performances are reported in Table 6.



R = ^{i}Pr, R' = H, **41;** R = Et, R' = H, **42**; R = Me, R' = H, **43**; R = R' = Me, **44**

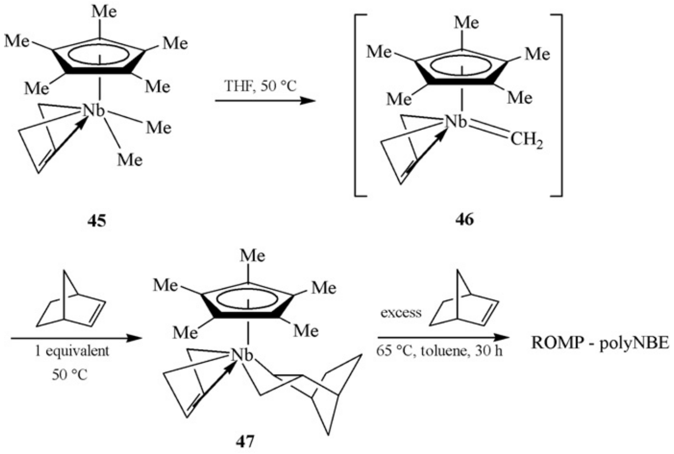
Complex **41**, containing the most sterically demanding substituents on the N-aryl ring, shows the highest activity (70 $g_{polymer}(mmol\,Nb)^{-1}\,bar^{-1}\,h^{-1}$) and the corresponding tantalum complexes (R = ^{i}Pr, R′ = H) are less active than the niobium one. The polyethylenes obtained with compounds **41**–**44** show broad molecular weight distributions (suggesting multiplicity of active sites) and high melting points (130–140 °C), indicating a linear structure.

3. Niobium catalysts for cyclic olefin polymerization

The polymerization of cyclic olefins catalyzed by niobium or tantalum derivatives has been rarely studied and the data reported in the literature generally refer to the polymerization of bicyclo[2.2.1]hept 2-ene, better known as norbornene (NBE).

NBE and its derivatives can be polymerized by three different ways, namely ring opening metathesis polymerization (ROMP), cationic or radical polymerization and addition polymerization [56]. NBE is an extremely reactive strained cyclic olefin and its metathesis polymerization is well-studied for investigating potential new ROMP catalysts. The polymer obtained by the metathetic polymerization is a polyalkenamer still containing double bonds in the polymer backbone, Scheme 6.

At variance with the results obtained with ethylene (tantalum is generally less active than niobium, the activity of both metals being rather low, see Section 2), several tantalum complexes are active in the ROMP polymerization of norbornene. This has been related to the higher reactivity of the cyclic olefin with respect to ethylene. In 1997, Mashima and coworkers reported that the dimethylniobium(III) complex **45**, obtained by the sequence of reaction reported in Scheme 7, is a thermally unstable compound which easily generates the methylidene intermediate **46** (via α-elimination of methane) which, in the presence of NBE, affords the thermally stable NBE complex **47**, which has been fully characterized (X-ray structure). Compound **47** is a catalyst for the ROMP of norbornene [23], Scheme 7. The polymer (M_n = 2900, M_w/M_n = 4.78) has a high *cis* content (91%); no detailed investigations about the optimization of the polymerization conditions has been described.

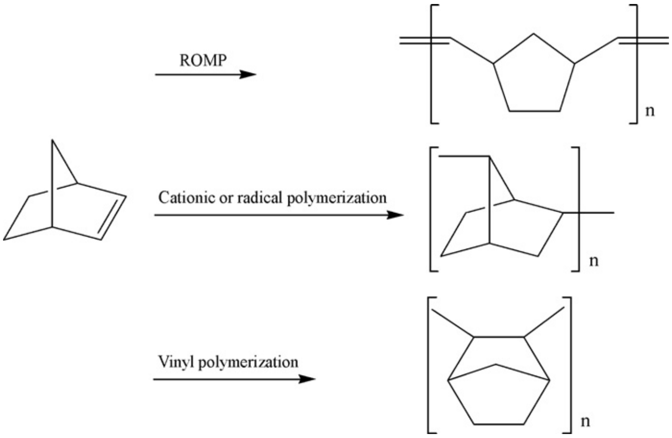


Scheme 7. Proposed mechanism for the ROMP polymerization of NBE catalyzed by NbCp*Me$_2$(η^4-C$_4$H$_6$) [23].

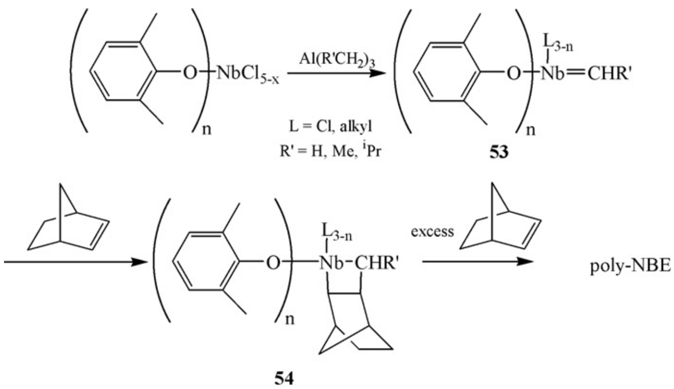
The catalytic activity of NbCl$_5$ in the presence of Me$_2$AlCl as co-catalyst for ROMP of norbonene has been claimed in a Japanese patent [57] and Rooney and coworkers have also reported that the combination NbCl$_5$/MAO or MAO alone show some catalytic activity to give ROMP poly-NBE [58]. In both cases, an optimization of the reaction conditions was not reported and the data are insufficient in order to estimate the catalytic activity of these systems.

Recently Nakayama and coworkers have carried out an investigation on the catalytic activity of the bis(imino)pyridine derivatives of niobium(III) **41**–**44** activated by aluminium co-catalysts [55], but their activity was very low (Table 7).

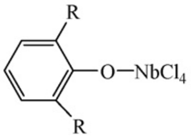
Much better results were obtained by the same research group with niobium(V) complexes containing phenolato **48**–**49** [59], biphenolato-, **50**–**51**, or bis(naphtholato), **52** ligands in the presence of alkyl aluminium co-catalysts [60]. Selected data on the catalytic performance observed in the presence of different alkyl aluminium co-catalysts are reported in Table 8. Working in toluene at room temperature a ROMP activity up to 1700 kg of polymer/(mol of catalyst x hour) afforded polymers with high molecular weight and slightly *trans*-rich structure. A tentative mechanism based on the formation of alkylidene species **53** and of metallacyclobutane intermediates **54** has been given [59], Scheme 8.



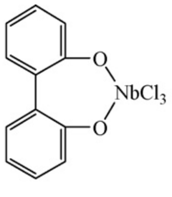
Scheme 6. Polymerization modes of NBE.



Scheme 8. Proposed mechanism for the ROMP polymerization of NBE catalyzed by niobium alkoxide compounds [59].



R = H, **48**; Me, **49**



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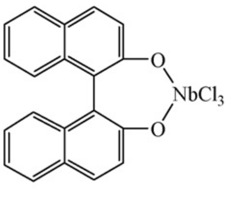

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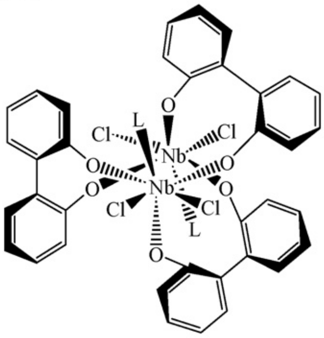

$Nb_2Cl_4(bisphenolato)_3(MeCN)_2$, **51**

In the search of cheap and easy to synthesize compounds to be used to obtain ROMP poly-NBE, Raspolli and coworkers very recently have used niobium(V) N,N-dialkylcarbamates $Nb(O_2CNR_2)_5$, R = Et (**55**), Me (**56**) in the presence of aluminium co-catalysts as promoters [61]. These rather cheap, easy to synthesize and easily soluble niobium complexes [62] appeared good candidates as catalytic precursors for NBE polymerization, due to the well known coordination flexibility of the N,N-dialkylcarbamato ligands, which are able to stabilize several metal oxidation states (from +5 to +2 in the case of niobium) [63], thus allowing the formation of the active catalytic species. Selected results obtained in NBE polymerization are reported in Table 9.

These novel catalytic systems showed low activity in toluene but were very active in a more polar solvent such as chlorobenzene. Compound **55** in the presence of methylalumoxane catalyzes the ROMP of norbornene with a highly remarkable activity [up to 29,000 $g_{polymer}(mmol\ Nb)^{-1}\ h^{-1}$]. The activity reached under these conditions is the highest one reported until now for niobium catalysts and represents a remarkable result when compared to the performances of the other metal catalysts employed for ROMP [64] which require more complex preparative pathways.

When **56** was used as precursor, a decrease of the activity with respect to **55**-based systems was found (compare entries 66, 67

Table 7

Ring opening metathesis polymerization (ROMP) of norbornene catalyzed by the niobium complexes **41**–**44** activated by aluminium co-catalysts[a] [55].

Entry	Nb precursor	Co-catalyst	Al/Nb (mol/mol)	A^b	$M_n \times 10^{-4}$	M_w/M_n[c]	Trans (mol%)
50	**41**	Et_3Al	1	0.3	34	1.96	55
51	**41**	MMAO	100	0.1	17	1.70	75
52	**42**	Et_3Al	1	0.1	21	3.22	45
53	**43**	Et_3Al	1	0.1	28	2.56	50
54	**44**	Et_3Al	1	0.1	38	1.93	49

[a] Reaction conditions: precursor, 0.02 mmol; solvent, toluene; *T*, 25 °C; time, 24 h.

[b] Activity: $g_{polymer}(mmol\ Nb)^{-1}\ h^{-1}$.

[c] Determined by GPC.

Table 8

Ring opening metathesis polymerization (ROMP) of norbornene catalyzed by the niobium complexes **48**–**52** activated by aluminium co-catalysts[a] [60].

Entry	Nb precursor	Co-catalyst	Time (min)	A^b	$M_n \times 10^{-4}$	M_w/M_n[c]	Trans (mol%)	Ref.
55	$NbCl_5$	Et_3Al	360	0.7	71	1.77	53	[59]
56	$NbCl_5$	Me_3Al	1	1700	72	2.23	56	[59]
57	**48**	Et_3Al	180	1.7	69	2.43	57	[59]
58	**48**	Me_3Al	1	1700	55	1.96	54	[59]
59	**49**	Et_3Al	360	2.2	60	2.20	55	[59]
60	**49**	Me_3Al	1	1700	73	2.26	54	[59]
61	**50**	Me_3Al	12	34	66	1.52	56	[60]
62	**51**	Me_3Al	12	25	107	1.68	55	[60]
63	**52**	Me_3Al	12	37	93	1.75	57	[60]

[a] Reaction conditions: precursor, 20 μmol; solvent, toluene; Al/Nb, 1 mol/mol; *T*, 25 °C.

[b] Activity: $g_{polymer}(mmol\ Nb)^{-1}\ h^{-1}$.

[c] Determined by GPC.

Table 9

Ring opening metathesis polymerization (ROMP) of norbornene catalyzed by niobium(V) carbamates, **55**–**56**, activated by aluminium co-catalysts[a] [61].

Entry	Nb precursor	Co-catalyst	Al/Nb (mol/mol)	Time (min)	*T* (°C)	A^b	Trans (mol%)
64	**55**	MAO	50	5	25	7,400	52
65	**55**	MAO	50	1	25	20,500	51
66	**55**	MAO	500	1	25	24,100	46
67	**55**	MAO	500	1	50	29,200	54
68	**55**	MAO	500	5	0	2,300	39
69	**55**	Me_3Al	5	5	25	310	43
70	**56**	MAO	50	1	25	7,800	53
71	**56**	MAO	500	1	25	8,600	55
72	**56**	MAO	500	1	50	9,700	56

[a] Reaction conditions: precursor, 2.2 μmol; 20.7 ml of 20 wt.% norbornene solution in chlorobenzene.

[b] Activity: $g_{polymer}(mmol\ Nb)^{-1}\ h^{-1}$.

and 68 with 61, 62 and 63, respectively), although the polymer had analogous characteristics. These lower performances may be related to the decreased steric hindrance of the $[O_2CNMe_2]^-$ ligand with respect to the ethyl-substituted one [63]. It is in fact well known that the "overpopulation" of the coordination sphere of the metal helps the α-hydrogen elimination of an alkyl intermediate to give the alkylidene compound responsible of the activation of NBE to give ROMP polymer [23,65].

4. Conclusions

More than 50 years have passed since the seminal works by Ziegler and Natta and still researchers look for the "best" olefin polymerization catalysts. The enormous effort has allowed the collection of much data also for those elements which are quite inactive in promoting olefin polymerization.

A class of these compounds belongs to the Group 5 metals, vanadium excluded. As a matter of fact, it is generally observed that the vanadium complexes are more active than the corresponding heavier congeners, i.e., niobium and tantalum. This may be ascribed to the known increase of metal–ligand bond energy on going down a group of transition elements and to the decrease of the metal/ligand exchange rate in the same direction [66].

In this review we have summarized the present situation regarding the use of niobium complexes as catalysts for the polymerization of olefins, making specific reference to ethylene and norbornene. As far as norbornene is concerned, we have used this occasion to report a new type of catalytic precursor based on N,N-dialkylcarbamates $[O_2CNR_2]^-$, a class of ligands that has been studied in detail by Calderazzo [63].

Acknowledgment

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