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Fluoride adducts of niobium(V): Activation reactions and alkene polymerizations

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ABSTRACT

Fluoride coordination derivatives of niobium(V) were tested for their activation capabilities with respect to acetone and to olefins. Activation of acetone (formation of mesityloxide) was observed with $NbF_4(OMe)$. Several fluoride coordination derivatives of niobium(V) of different nature (neutral or ionic) and nuclearity, i.e. NbF_5L [L = Et_2O, **4**, thf, **5** (thf is tetrahydrofuran), MeOH, **6**, EtOH, **7**], $(NbF_4L_2)(NbF_6)$ [L = dmf, **8** (dmf is dimethylformamide), dme, **9** (dme is dimethoxyethane)], $(NbF_4L_4)(NbF_6)$ [L = thf, **10**, Et_2O, **11**, MeCN, **12**], $[S(NMe)_3][NbF_6]$, **13**, NbF_4OMe, **1**, NbF_4OPh, **3**), $NbF_3(OPh)_2$, **14**, $NbF_2(OPh)_3$, **15** and $NbF_2(OEt)_3$, **16**, promoted the polymerization of ethylene using $AlMe_3$-depleted methylaluminoxane as cocatalyst. Highly linear polyethylene was obtained. Compound **3**, upon activation with methylaluminoxane, promoted ring-opening metathesis polymerization (ROMP) of norbornene, affording polymers with a slight excess of *trans* content.

1. Introduction

As a consequence of the exceptionally strong M–F bonds [1], transition metal fluorides were considered for long time as synthetically and catalytically inert [2]. Nevertheless, the study of the chemistry of group 4 fluorides has provided several excellent examples clearly demonstrating that the strong M–F bond does not preclude their use in catalysis. For example, $TiCp'F_3$ (Cp′ = substituted cyclopentadienyl ring) [3] or $TiCpCl_2(OR)/BF_3$ [4] derivatives are more active as ethylene polymerization catalyst than the corresponding chloride. Similarly, the difluoride Zr[*rac*-1,2-ethylene-1,1′-bis(tetrahydroindenyl)F_2 is more active than the analogous chloride in the presence of Al^iBu_3 (or AlH^iBu_2) [5]. On the other hand, examples do not lack of metal fluoride species behaving as less active catalysts with respect to the corresponding chlorides [6].

In spite of the belief that *niobium and tantalum live in the shadow of metal complexes of Group 4* [7], niobium and tantalum pentahalides, MX_5, have found increasing application in effective metal-directed organic synthesis [8,9].

In this context, also the pentafluorides of niobium and tantalum have found application in a variety of processes [10], including fluorination [11], alkylation [12] and ring opening polymerizations [13], sometimes showing reactivities markedly different from the corresponding heavier halides [10,13].

The chemistry of MX_5 with limited amounts of oxygen compounds has been elucidated in the very last years [8,14]. Different types of coordination adducts (neutral or ionic) have been isolated upon reaction of controlled amounts of oxygen donors with NbX_5 and a significant difference of behavior has been noticed when moving from fluoride to the heavier halides. In general, organic halides are generated in the course of the activation processes involving NbX_5 (X = Cl, Br, I), while NbF_5 is able to activate several oxygen-containing molecules without the formation of organic fluorides [15]. Such a behavior is generally related to the increase of the bond energy with decreasing the atomic weight of the halide [8].

It has been demonstrated that simple coordination adducts of $NbCl_5$ with oxygen ligands are active catalysts in a series of polymerization reactions, providing generally greater performances with respect to $NbCl_5$ [16].

On account of this state of art, we decided to investigate the possible activation reactions of some of the recently prepared NbF_5 derivatives [17,19], including some fluoride-alkoxide(aryloxide) compounds of general formula $MF_{5-n}(OR)_n$, obtained straightforwardly from MF_5 [18][2] via reactions with trimethylsilyl ethers [19].

The results, including the polymerization of ethylene and the ROMP of norbornene, are reported in this paper.

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[2] The pentafluoride of niobium(V) has tetranuclear structure in the solid state (ref19). For sake of simplicity, the empirical formula NbF_5 has been used throughout the present paper.

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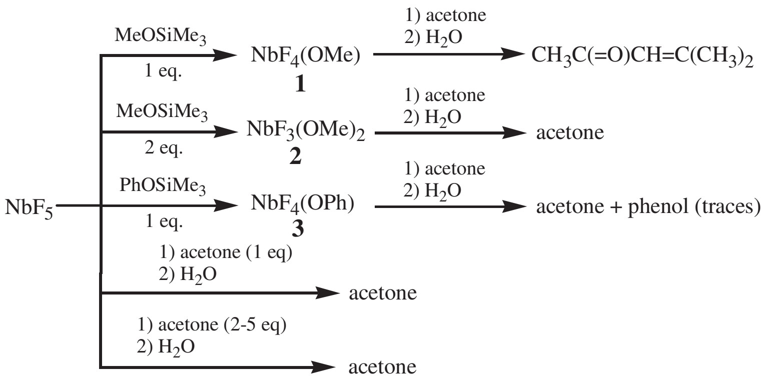
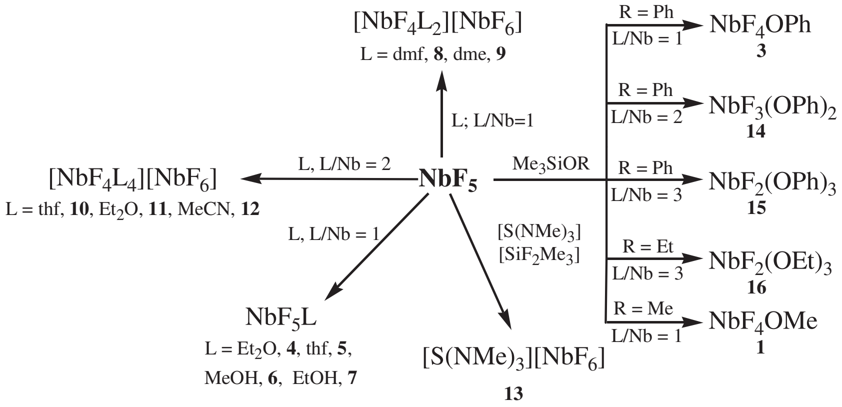


Scheme 1. Comparative view of the reactivity of NbF_5, $NbF_4(OMe)$ and $NbF_3(OMe)_2$ with acetone.



Scheme 2. Synthesis of niobium fluoride adducts.

2. Results and discussion

Reactivity of $NbF_n(OR)_{5-n}$ ($n = 4$, R = Me, **1**; Ph, **3**; $n = 3$; R = Me, **2**) with acetone.

According to our recent results [19], fluoride–alkoxides of Nb(V), $NbF_n(OR)_{5-n}$, have different nuclearities depending on the fluorine content. Thus $NbF_4(OPh)$, **3**, is probably tetranuclear both in the solid state and in chlorinated solvent, while $NbF_4(OMe)$, **1**, exists as mixture of tetra- and trinuclear forms. $NbF_3(OPh)_2$ has got a trinuclear structure, and $NbF_2(OR)_3$ (R = Et, **15**; R = Ph, **16**) are presumably dinuclear.

In view of the availability of the newly prepared fluoride-alkoxide complexes [19], we decided to investigate the reactivity of some of them with an oxygen donor such as acetone. Hence slow darkening of the mixtures was noticed after addition of acetone to $NbF_4(OMe)$ (acetone/Nb molar ratio = 1), in CD_2Cl_2. The ^1H and ^{13}C NMR spectra of the reaction solutions consisted of complicated patterns. Otherwise the corresponding ^{19}F NMR spectra revealed the presence of significant amounts of the $[NbF_6]^-$ ions (see Section 4, NMR studies), suggesting that the addition of the ketone determines the disruption of the polynuclear units of the alkoxides [19].

Upon hydrolysis of the mixture, $Me_2C{=}CHC({=}O)Me$ (mesityl oxide) was recognized as prevalent species from $NbF_4(OMe)$/acetone/H_2O[3]. The presence of some singlets around 6.5 ppm, in the ^1H NMR spectra of the mixtures $NbF_4(OMe)$/acetone, supports the idea that mesityl oxide forms directly as result of the interaction between acetone and the fluoride alcoholate complex.

When acetone was allowed to react with $NbF_4(OPh)$ and $NbF_3(OMe)_2$ in dichloromethane, acetone/phenol and acetone, respectively, were the species which could be clearly recognized after hydrolysis of the reaction mixtures.

These findings reveal that the nature of the R group (i.e. Me or Ph) and the nuclearity of the metal influence the reactivity with acetone. More specifically, $NbF_4(OMe)$ has revealed to be a highly acidic species, able to promote C—H activation of acetone in mild conditions, to give the C—C coupling product mesityl oxide (see Scheme 1). It is noteworthy that the analogous C—H activation is not verified by using NbF_5 [17].

Olefin polymerization reactions

A variety of well-soluble niobium compounds obtained by high-yield reaction of NbF_5 with controlled amount of Lewis bases was tested in the ethylene polymerization. The employed compounds are reported in Scheme 2 and include neutral mononuclear (**4–7**), ionic (**8–13**), and polynuclear species (**1**, **3**, **14–16**).

The polymerization reactions have been carried out under the same experimental conditions successfully employed for analogous niobium(V) chloride derivatives [20], i.e. using DMAO as cocatalyst (see Table 1). Although NbF_5 is inactive in ethylene polymerization, the mononuclear complexes **4–7** are able to produce polyethylene with low to moderate activity, thus suggesting that the breaking of the tetranuclear structure of NbF_5 [18], by addition of a neutral molecule (L) to form soluble NbF_5L adducts, represents a straightforward approach to enhance the catalytic performances of the metal species. Nevertheless, $NbF_5(OEt_2)$, **4**, resulted ineffective in contrast with what observed with the chlorinated adduct $NbCl_5(OEt_2)$ [21], the lat-

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[3] Hydrolysis of $CDCl_3$ solutions of $[NbF_4(acetone)_4][NbF_6]$ and $NbF_5(acetone)$ gave acetone in nearly quantitative yield.

Table 1
Results of ethylene polymerization runs with precatalysts **1**–**16**.[a]

Run	Precursor	Activity[b]	M_w (Da)	PDI[c]	T_m (°C)
1	$NbF_5(OEt_2)$, **4**	–	–	–	–
2	$NbF_5(thf)$, **5**	55	102 000	13.5	133
3	$NbF_5(MeOH)\cdot$ **6**	22	255 000	12.1	133
4	$NbF_5(EtOH)$, **7**	20	110 000	15.5	132
5	$[NbF_4(dmf)_2\ [NbF_6]$, **8**	32	463 000	13.7	134
6	$[NbF_4(dme)_2][NbF_6]$, **9**	trace	–	–	
7	$[NbF_4(thf)_4][NbF_6]$, **10**	10	101 000	14.6	133
8	$[NbF_4(OEt_2)_4][NbF_6]$, **11**	45	220 000	13.2	133
9	$[NbF_4(NCMe)_4][NbF_6]$, **12**	–	–	–	
10	$[S(NMe_2)_3][NbF_6]$, **13**	–	–	–	
11	$NbF_4(OMe)$, **1**	0.3	–	–	133
12	$NbF_4(OPh)$, **3**	60	147 000	10.3	133
13	$NbF_3(OPh)_2$, **14**	41	186 000	11.5	133
14	$NbF_2(OPh)_3$, **15**	20	210 000	11.7	134
15	$NbF_2(OEt)_3$, **16**	trace	–	–	–
16	NbF_5	trace	–	–	–
17	$NbCl_5$[d]	11	136 000	–	132.3

[a] Reaction conditions: precursor = 40 μmol; DMAO/Nb molar ratio = 600; T = 50 °C; P_{C2H4} = 0.1 MPa; t = 15 min; solvent: chlorobenzene (50 mL); re-activator: 1,2-dichloroethane (2 mmol).
[b] Activity expressed as $kg_{polymer} \times mol_{Nb}^{-1} \times h^{-1} \times bar^{-1}$.
[c] Polydispersity index.
[d] From Ref. [28].

ter showing an activity of 95 $kg_{polymer}\ mol_{Nb}^{-1}\ h^{-1}\ bar^{-1}$ [20]. This observation may be attributed to the fact that ethyl ether is a Lewis base not strong enough to fragment the tetranuclear structure of NbF_5 as instead happens in the case of the dinuclear $NbCl_5$ [18]. On the other hand, the ionic diethylether adduct **11** shows one of the highest activities reported in Table 1. An opposite trend is observed when going from **5** to **10** (neutral and ionic thf adducts, respectively), probably due to the stronger coordinating power of thf with respect to Et_2O [22]. The easier accessibility of the monomer to the hexacoordinated central metal atom in **5** may explain the higher activity observed with **5** respect to **10**, that contains octacoordinated niobium atom. Moreover, the activity exhibited by **10** is reasonably due to the cation only, in consideration of the fact that the $[NbF_6]^-$ salt **13** does not produce polymer.

We also tested the catalytic activity of the known dme-octacoordinated cation **9** [15a], and the acetonitrile adduct **12** reported here for the first time. Both compounds are not effective in ethylene polymerization, possibly for steric reasons due to the presence of two bidentate dme ligands (compound **9**) or for some detrimental effects caused by the unsaturated nitrogen ligand (compound **12**).

Finally, in view of the good outcomes previously obtained with mixed chloride-alkoxide niobium compounds [16], some fluoride-alkoxides [19] have been tested for ethylene polymerization. Thus, the phenoxides **3**, **14**, **15** have provided some polymer, the activity increasing on increasing the relative fluoridecontent. This is in agreement with the observation that when the electrophilicity of the metal center increases, a relatively positive niobium center will exhibit high activities for ethylene polymerization [23]. Otherwise, the presence of ethyl group in the place of phenyl (compare **15** with **16**) is sufficient to cause a drop in the activity.

Molecular weight distribution (M_w/M_n) data revealed in every case broad polydispersity and multimodal distribution, thus indicating the non-single-site nature of the catalyst.

The melting points (T_m) of poly(ethylene)s were determined by DSC analysis. The melting point ranges between 132 and 134 °C, typical of high density polyethylene. The FT-IR spectrum of polymeric samples displays the typical bands corresponding to the high density polyethylene [24].

Table 2
ROMP of norbornene with compounds **3** and with NbF_5.[a]

Run	Precursor (μmol)	t (min)	Activity[b]	*Trans* (mol.-%)
1	**3** (22)	5	56	n.d.
2	**3** (2.2)	5	174	53
3	**3** (2.2)	1	272	54
4	NbF_5 (2.2)	5	93	48
5	$NbCl_5$ (2.2)[c]	5	1250	47

[a] Reaction conditions: 20.7 mL of 20 wt.% norbornene solution in chlorobenzene; MAO/Nb molar ratio = 500; T = 50 °C; cocatalyst: MAO.
[b] Activity expressed as $kg_{PNB} \times mol_{Nb}^{-1} \times h^{-1}$.
[c] From Ref. [25].

The catalytic behavior of compound **3**, which presented the highest activity in ethylene polymerization, was also studied in a limited number of norbornene polymerization reactions. The reaction conditions were selected on the basis of our previously reported experiments [25]. When the precursor **3** was treated with MAO at 50 °C for 5 min of reaction time, (run 1, Table 2), the resulting catalytic system gave a moderate activity (56 $kg_{PNB}\ mol_{Nb}^{-1} \times h^{-1}$). Polymer characterization revealed that the polymerization mechanism took place only by ring-opening metathesis polymerization (ROMP).

The decrease of precatalyst concentration up to 2.2 μmol increased the catalytic activity almost three-times. A further remarkable improvement of the productivity was ascertained when reaction time was reduced to 1 min (run3, Table 2): the value was reached to 272 $kg_{PNB}\ mol_{Nb}^{-1} \times h^{-1}$. The enhanced performance at shorter reaction time can be attributed to the much lower viscosity of the reaction medium, which allows a more efficient mixing, reducing diffusion limitations.

In order to confirm the importance of the phenoxide moiety on the polymerization behavior, NbF_5 was employed as precursor for ROMP carried out under the same polymerization conditions (run 4, Table 2). As it can be seen from the data of Table 2, the productivity of NbF_4OPh is well higher than that obtained with NbF_5 under the same experimental conditions.

Swelling of polymer samples in $CDCl_3$ allowed to clarify the microstructure of the polymers. In all cases the ^{13}C NMR spectra indicate that the polymer has an almost random sequence of *cis* and *trans* double bonds [25] with a slight higher content of the latter.

3. Conclusion

Fluoride coordination derivatives of niobium(V) have been tested for their activation capabilities with respect to acetone and to olefins. Activation of acetone (formation of mesityloxide) has been observed with $NbF_4(OMe)$, thus suggesting that this fluoride-alcoholato complex probably has an acidic character stronger with respect to that exhibited by the parent pentafluoride and pentachloride.

Fluoride derivatives of different nature (neutral or ionic) and nuclearity have been tested as catalytic precursors in the polymerization of ethylene. The best results reported herein in terms of activity (compounds **3**, **5**) toward ethylene polymerization are less valuable with respect to those obtained with analogous chloride-containing species. However, they are interesting in the context of olefin polymerization catalyzed by niobium precursors, on consideration of the fact that no studies have been reported hitherto in this field concerning niobium fluoride derivatives. Moreover, compound **3** catalyzed the ROMP of norbornene with moderate to high activities and gave polymer samples with slightly higher *trans* content.

4. Experimental

4.1. General

All manipulations of air and/or moisture sensitive compounds were performed under atmosphere of pre-purified argon using standard Schlenk techniques. The reaction vessels were oven dried at 150 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. NbF_5 was the commercial product (Aldrich) of the highest purity available, stored under Argon atmosphere as received. Solvents and compounds used as ligands were commercial products (Aldrich) of the highest purity available. Ethylene (>99%; Rivoira) was used as received. Norbornene (Aldrich) was distilled from CaH_2 and then dissolved in chlorobenzene in appropriate concentrations. Compounds **4** [21], **5**–**7**, **10**, **11**, **13** [17], **8** [26], **9** [15], **1**, **3**, **14**–**16** [19] were prepared according to the literature. Infrared spectra were recorded at 293 K on a FT IR Spectrum One Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. NMR measurements were recorded on Varian Gemini 200BB instrument at 293 K, unless otherwise specified. The thermal behavior of polyethylene was examined with a Perkin Elmer Pyris Diamond DSC at a standard heating/cooling rate of 10 °C min^{-1}, under nitrogen flow. The reported melting temperature values refer to the second heating scan. SEC measurements were carried out with a high temperature Waters GPCV2000 system equipped with a differential refractometer as concentration detector. The experimental conditions consisted of three PL Gel Olexis columns, *o*-dichlorobenzene as the mobile phase, 0.8 mL min^{-1} as the flow rate and a column temperature of 145 °C. The calibration of the SEC system was constructed using 18 narrow MWD polystyrene standards with molar weights ranging from 162 to 5.6×10^6 g mol^{-1}.

The ethylene polymerization reactions were carried out by adopting the optimized experimental conditions used in the ethylene polymerization by $NbCl_4[\kappa^2\text{-}O(CH_2)_2OMe]$ and analogous Nb(V) chloro-alkoxide complexes [22]. Dry methylaluminoxane (DMAO) was prepared by removing trimethylaluminium and toluene from commercial MAO (Sigma Aldrich, toluene solution 10% w/w) in vacuo at 30 °C for 6 h, followed by repeated slurring in heptane. The colorless solid was recovered by filtration and dried in vacuo at room temperature [27]. Norbornene polymerization reactions were carried out as previously reported [25].

4.2. Preparation of $[NbF_4(MeCN)_4][NbF_6]$ (**12**)

A suspension of NbF_5 (0.150 g, 0.798 mmol) in dichloromethane (12 ml) was treated with MeCN (1.70 mmol). The mixture was stirred for 3 h, then the resulting pale-yellow solution was dried under vacuo. The residue was washed with hexane (2×10 mL), thus compound **12** was obtained as a colorless sticky solid. Yield 0.179 g, 83%. ^1H NMR ($CDCl_3$, 298 K): $\delta = 2.57$ (s, Me) ppm. ^{13}C NMR ($CDCl_3$, 298 K): $\delta = 101.2$ (NCMe), 2.3 (Me) ppm. ^{19}F NMR ($CDCl_3$, 298 K): $\delta = 164.3$ (s-br, $[NbF_4]^+$), 112.3 (br, $[NbF_6]^-$) ppm.

4.3. Reactivity of $NbF_4(OMe)$, **1**, and $NbF_3(OMe)_2$, **2**, with acetone

In an NMR tube, a colorless solution of the metal compound (**1** or **2**, 0.50 mmol) in CD_2Cl_2 (0.60 mL) was added of dry acetone (0.50 mmol). The tube was sealed, shaken in order to homogenize the content, and stored at room temperature for 18 h. Turning of the color of the mixture to dark red was observed. The solution was analyzed by NMR. $NbF_4(OMe)$/acetone: $\delta(^1H$, 198 K) = 9.05 (br), 6.93, 6.82, 6.58 (major), 4.59, 4.52 (major), 3.78 (major), 3.69, 2.78, 2.69, 2.64, 2.50, 2.42, 2.36 (major) ppm; $\delta(^{19}F$, 198 K) = 103 (decet, major, $[NbF_6]^-$), 92.0 (s), 72.7 (s) ppm. $NbF_3(OMe)_2$/acetone: $\delta(^1H$, 298 K) = 8.39 (br), 4.08 (s, 3 H), 2.29 (s, 3 H) ppm; $\delta(^{19}F$, 198 K) = 103 (decet, $[NbF_6]^-$), 92.0 (s, major), 70.6 (s, br) ppm.

An aliquot of the solution obtained by $NbF_4(OMe)$/acetone was dried under vacuo, thus the resulting red residue was analyzed by IR spectroscopy. The spectrum showed bands at 2965w, 1608m, 1520 m, 1445m, 1406m, 1382m, 1109s, 986s, 880br-vs 716br-vs cm^{-1}.

Mesityl oxide was detected by NMR as largely prevalent species after hydrolysis of the reaction mixtures $NbF_4(OMe)$/acetone; acetone was the only species which could be clearly recognized after hydrolysis of the reaction mixtures $NbF_3(OMe)_2$/acetone.

4.4. Reactivity of $NbF_4(OPh)$, **3**, with acetone

The reaction of **3** (0.43 mmol) with dry acetone (0.43 mmol) was conducted in CD_2Cl_2 (0.60 mL) in an NMR tube. The tube was sealed, shaken in order to homogenize the content, and stored at room temperature for 18 h. The solution was analyzed by NMR. $NbF_4(OPh)$/acetone: $\delta(^1H$, 198 K) = 7.26, 7.08, 6.88 (Ph); 2.21 (CH_3) ppm; $\delta(^{13}C$, 198 K) = 210.1 (CO); 155.9, 129.5, 128.1, 120.4, 115.3 (Ph); 30.6 (CH_3) ppm. $NbF_4(OPh)$/acetone (after hydrolysis): $\delta(^1H$, 198 K) = 7.26, 6.93, 6.86 (Ph); 6.14(OH); 2.19 (CH_3) ppm; $\delta(^{13}C$, 198 K) = 208.1 (CO); 156.0, 127.8, 120.3, 115.2 (Ph); 30.7 (CH_3) ppm.

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