*Pure Appl. Chem.*, Vol. 81, No. 7, pp. 1205–1215, 2009. doi:10.1351/PAC-CON-08-08-05 © 2009 IUPAC, Publication date (Web): 29 June 2009

# [ONNO]-type amine bis(phenolate)-based vanadium catalysts for ethylene homo- and copolymerization\*

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Abstract: The synthesis and solution and solid-state structural characterization of a family of amine bis(phenolate) [ONNO]-vanadium complexes is reviewed. These compounds have oxidation states ranging from vanadium(II) to vanadium(V), and were evaluated as olefin polymerization catalysts. In association with  $EtAlCl_2$  cocatalyst, we studied the homopolymerization of ethylene, propene, and 1-hexene, as well as the copolymerization of ethylene with  $\alpha$ -olefins (1-hexene, 1-octene) and cycloolefins (norbornene, cyclopentene). Some of these catalysts were shown to produce copolymers with a good activity and comonomer content.

Keywords: vanadium; amine bis(phenolate); polymerization; copolymerization; olefins.

## INTRODUCTION

Olefin-based polymers, such as polyethylenes, polypropylenes, ethylene/ $\alpha$ -olefin copolymers, and elastomers are now materials indispensable to our modern life. Millions of tons of these polymers are produced per year, most of them using the multi-sited heterogeneous Ziegler–Natta catalysts (TiCl<sub>4</sub> supported on MgCl<sub>2</sub>). Owing to the breakthrough development of metallocene and constrained-geometry single-site catalysts, "tailor-made" (co-)polymers with improved properties due to (i) controlled molecular weight, tacticity, comonomer content, and distribution and (ii) improved molecular weight distribution, are under industrial production worldwide [1,2].

The copolymerization of ethylene with  $\alpha$ -olefins is a common means of generating polyethylenes of controlled crystallinity and density. These polymers are known as linear low-density polyethylenes (LLDPEs). The introduction of short-chain branches originated from the comonomer decreases the crystallinity and melting temperature of the copolymer as the co-units interfere with crystallization and reduce the size of crystallites. Cycloolefin copolymers are also interesting materials, for example, poly(ethylene-*co*-norbornene)s possess rather interesting properties (high glass transitions, good chemical and heat resistance, and excellent transparency) that make them promising in particular for their potential applications in optoelectronic.

In recent years, new trends in olefin coordination polymerization have been directed toward the use of many transition metals (both early and late transition metals) and in association with various noncyclopentadienyl ligands [3–5]. For example, chelating diamide [6–10], dialkoxide [11–13], or

<sup>\*</sup>Paper based on a presentation at the 6<sup>th</sup> International Symposium on Chemistry and Biological Chemistry of Vanadium, 17–19 July 2008, Lisbon, Portugal. Other presentations are published in this issue, pp. 1187–1330.

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phenoxyimine [16,17] ligands have received considerable attention as rigid supporting environments for group 4 metal complexes, resulting in the emergence of a great deal of novel and useful chemistry, including the discovery of highly active olefin polymerization precatalysts. Among these new ligands, chelating dianionic [ONNO]-type amine bis(phenolate) ligands associated with titanium and zirconium complexes have proven as highly active 1-hexene polymerization catalysts, and in some cases even isospecific living polymerization was possible [11].

Vanadium-based Ziegler–Natta catalyst systems have been known for about half a century [17], and V(acac)<sub>3</sub> is currently employed in the production of EP (ethylene-propylene) and EPDM (ethylenepropylene-diene monomer) elastomers. Their use presents a number of interesting advantages over group 4 metal catalysts [18]: (i) the synthesis of high-molecular-weight polymers with narrow polydispersity, (ii) the preparation of ethylene/ $\alpha$ -olefin copolymers with high  $\alpha$ -olefin incorporation, and (iii) and the preparation of syndiotactic polypropylene. However, vanadium-based catalysts generally suffer from a lower activity. The major reason for this is their deactivation during the polymerization process, probably due to reduction of catalytically active vanadium species to low-valent, less active, or inactive species [18].

In our group, we have a long-term interest in the study of vanadium chemistry with various supporting ligands [19,20], and in particular of vanadium complexes (as well as their related group 4 metal complexes) for olefin polymerization. We have recently used ancillary diamido ligands with sterically demanding protecting groups [10] or imido ligands [27] on vanadium(IV) complexes as a way to overcome the problem of catalyst deactivation by stabilization of the formal oxidation state of the vanadium center. Following this approach, we have recently introduced the amine bis(phenolate) [ONNO]-type ligand (Fig. 1) as a supporting ligand for vanadium complexes, and we have evaluated their ethylene homo- and copolymerization activity [28–30]. It is the aim of this short review to summarize the synthetic routes we employed for the preparation of a family of [ONNO]-vanadium compounds, a brief summary of their solution and solid-state structures, as well as the olefin polymerization and copolymerization that were conducted with these catalysts.



Fig. 1 Synthesis of the [ONNO]H<sub>2</sub> proligand.

## AMINE-BIS(PHENOLATE)-VANADIUM COMPLEXES, SYNTHESIS, AND STRUCTURE

Vanadium complexes supported by the [ONNO] ligands at various oxidation states of the metal center were prepared and are described below according to their oxidation states. The synthesis of the amine bis(phenol) follows a Mannich condensation involving 2 equiv of the substituted phenol, formaldehyde, and the 2-dimethylamino-1-ethylamine in refluxing methanol, as illustrated in Fig. 1 [31].

## [ONNO]-vanadium(V) complexes

The protonolysis reaction between VO(NEt<sub>2</sub>)<sub>3</sub> and [ONNO]H<sub>2</sub> has proven to be difficult even under refluxing conditions in toluene. The direct metathesis reaction between VOCl<sub>3</sub> and the dipotassium salt of the ligand precursor K<sub>2</sub>[ONNO], conducted at low (-78 °C) or ambient temperature, leads to the formation of unidentified reduced vanadium species.

An entry to the [ONNO]-vanadium chemistry was successfully achieved by reacting the alkoxides VO(OR)<sub>3</sub> ( $R = {}^{i}Pr$ ,  ${}^{t}Bu$ , CH<sub>2</sub>CF<sub>3</sub>) with the bisphenol [ONNO]H<sub>2</sub> in toluene at room temperature (RT). The corresponding oxo-alkoxo complexes VO(OR)[ONNO] (1) [R =  ${}^{i}$ Pr (1a),  ${}^{t}$ Bu (1b), CH<sub>2</sub>CF<sub>3</sub> (1c)] were obtained in good yield (ca. 80 %) as dark blue solids (Fig. 2) [28]. Later, the synthesis of the *tert*-butyl substituted amine bis(phenolate) related complexes VO(OR)[ONNO<sup>*t*</sup>Bu] (R = Me, Et) was reported by Ali et al. from the reaction of VO(acac)<sub>2</sub> with [ONNO<sup>*t*</sup>Bu]H<sub>2</sub> in ROH under air [32].



Fig. 2 Synthesis of the [ONNO]-vanadium(V) complexes.

Addition of a strong donor (pyridine) to complex **1a** did not affect the <sup>1</sup>H NMR spectrum, suggesting that the side-arm NMe<sub>2</sub> group is strongly bound to the metal.

Although four different isomers could be expected for such octahedral complexes (cis and trans configurations of the phenolate rings, and isomers of the position of the oxo and alkoxo group), <sup>1</sup>H and <sup>51</sup>V NMR spectroscopic studies revealed the presence of only two isomers in solution (1 and 1') in a ratio major/minor 1:1' ~ 3:1. According to the proton NMR spectra, both isomers feature symmetry-related phenolate rings that exclude a cis geometry for those groups. Furthermore, the spectrum indicates an AB system for the Ar– $CH_2$ –N methylene units and a single signal for the OR group. Moreover, variable-temperature NMR studies (in toluene- $d_8$ , from -90 to +90 °C) on these systems did not show any significant differences, suggesting that the interconversion between the two isomers is not possible within the temperature range studied. Altogether, this indicates the formation of rigid, mononuclear  $C_{\rm s}$ -symmetrical complexes in which the phenoxy groups are in a *trans* configuration, and with oxo and alkoxo ligands being either in *cis* or in *trans* configuration to the tripodal N donor atom. We were able to determine the nature of each isomer by determining the spatial relations between different groups in the molecules with the help of selective nuclear Overhauser enhancement spectroscopy (NOESY) experiments. These experiments clearly indicate that the major isomer 1 is the *cis*-1 complex (the one that has the oxo group located in a *cis* position in respect to the tripodal amino N atom), whereas the minor isomer 1' is the *trans*-1 complex (the oxo is *trans* to the tripodal N atom).

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We were also interested in preparing complexes with a V–Cl bond (because the chloride ligand in these compounds could further be replaced by an alkyl group). We were able to prepare the corresponding VO(Cl)[ONNO] complex by three different routes (see Fig. 2). First, dark blue VO(Cl)[ONNO] was obtained by chlorination of the mixture of isomers VO(OR)[ONNO] (**1a–c**) with an excess of Me<sub>3</sub>SiCl. Second, VO(Cl)[ONNO] could be prepared from the isolable intermediate VO(N<sub>3</sub>)[ONNO] {obtained by addition of [ONNO]H<sub>2</sub> to VO(N<sub>3</sub>)<sub>2</sub>(O<sup>i</sup>Pr)}. But the most direct method involved the reaction of between equimolar amounts of [ONNO]H<sub>2</sub> and VO(Cl)(O<sup>i</sup>Pr)<sub>2</sub>.

VO(X)[ONNO] (X = Cl, N<sub>3</sub>) complexes have very similar spectroscopic features, and in this case, <sup>1</sup>H and <sup>51</sup>V NMR data revealed the formation of only one isomer, and were consistent with an isomer in which the phenolate rings are again in a *trans* configuration. The solution structure was also determined with the help of NOESY experiments and by comparison with the <sup>1</sup>H NMR pattern of both isomers of complexes **1a–c**. According to all these <sup>1</sup>H NMR studies, in solution, complexes VO(X)[ONNO] have the oxo group located in a *trans* position (to the tripodal N donor atom) and thus present the same features as of *trans*-**1** compounds, and then would have the same structural configuration.

## [ONNO]-vanadium(IV) complexes

Attempted synthesis of vanadium(IV) by reacting  $V(NR_2)_4$  (R = Me; Et) and the bisphenol proligand [ONNO]H<sub>2</sub> has met with limited success. By contrast, the amine elimination reaction between the bisazido complex  $V(N_3)_2(NMe_2)_2$  and [ONNO]H<sub>2</sub>, in tetrahydrofuran (THF), afforded the desired vanadium(IV) complex  $V(N_3)_2$ [ONNO] (**3**) in a moderate yield (40 %) (Fig. 3) [29]. This compound failed to go to completion when reacted with an excess of Me<sub>3</sub>SiCl (to replace the azides by chlorides) even under forcing conditions in refluxing toluene.



Fig. 3 Synthesis of the [ONNO]-vanadium(IV) complexes.

Next, we reacted  $[ONNO]H_2$  with an equimolar amount of the homoleptic alkoxide complex  $V(O^iPr)_4$  in toluene at RT for 2 h. The reaction yielded the new complex  $V(O^iPr)_2[ONNO]$  (4) with good yield (86 %) as a dark red microcrystalline solid (Fig. 3). The reaction of  $V(O^iPr)_2[ONNO]$  with 10 equiv of Me<sub>3</sub>SiCl in toluene at RT or 110 °C, afforded a mixture of the monochloro  $V(Cl)(O^iPr)[ONNO]$  and the dichloro  $V(Cl)(O^iPr)[ONNO]$  (5) derivatives that could be separated by selective crystallization. Complete chlorination of 4 was obtained by using larger excess of Me<sub>3</sub>SiCl

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(20 equiv) and under refluxing conditions (in toluene), to afford high yields of VCl<sub>2</sub>[ONNO] (96 %). Complex **5** is a good entry point to the synthesis of [ONNO]-vanadium compounds with additional V–C bonds, and dialkylation of **5** could produce VR<sub>2</sub>[ONNO] complexes (R = Me, CH<sub>2</sub>Ph, CH<sub>2</sub>SiMe<sub>3</sub>) [33].

All these [ONNO]-vanadium(IV) compounds have a  $d^1$  electronic configuration, both in solution and in the solid state. They present a well-resolved electron paramagnetic resonance (EPR) spectra with the characteristic octet pattern at ca. g = 1.97 that is expected for the interaction of an unpaired electron of V<sup>IV</sup> with the <sup>51</sup>V nucleus (I = 7/2). The susceptibility measurements are also in agreement with a  $d^1$ electronic configuration ( $\mu_{eff} = 1.77 - 1.82 \mu_{\rm B}$ ).

As already noted in the previous [ONNO]-vanadium(V) compounds, the sidearm NMe<sub>2</sub> group is sufficiently tightly bound to the metal center not to be displaced by strong donors (pyridine, PMe<sub>3</sub>): no change in the EPR signal could be evidenced (in particular, no coupling with the <sup>31</sup>P phosphorus nucleus of PMe<sub>3</sub> was observed).

## [ONNO]-vanadium(III) complexes

Treatment of V(acac)<sub>3</sub> with 1 equiv of [ONNO]H<sub>2</sub> gave the vanadium(III) complex V(acac)[ONNO] (6) in a 87 % yield (Fig. 4). V(acac)[ONNO] has a  $d^2$  electronic configuration and possesses an effective magnetic moment  $\mu_{eff}$  of 2.91  $\mu_B$  at 20 °C [31]. Slow addition of K<sub>2</sub>[ONNO] to a THF solution of VCl<sub>3</sub>(THF)<sub>3</sub> afforded yellow V(Cl)(THF)[ONNO] (7). As for 6, complex 7 is NMR-silent, and room-temperature magnetic susceptibility measurements gave a  $\mu_{eff}$  of 2.87  $\mu_B$ . Further alkylation of 7 gave the trivalent benzyl derivatives V(Bz)(THF)[ONNO] [33].



Fig. 4 Synthesis of the [ONNO]-vanadium(III) complexes.

## [ONNO]-vanadium(II) complexes

An entry to the [ONNO]-vanadium(II) chemistry was successfully achieved by reacting the vanadium(II) precursor VCl<sub>2</sub>(tmeda)<sub>2</sub> (tmeda *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) with equimolar amounts of K<sub>2</sub>[ONNO] in THF (RT, 2 h). Divalent V(tmeda)[ONNO] (**8**) was obtained as red crystals (Fig. 5) and is a high-spin  $d^3$ -paramagnetic, NMR-silent compound with an effective moment  $\mu_{eff}$  of 3.90  $\mu_{\rm R}$  at 20 °C [30].



Fig. 5 Synthesis of a [ONNO]-vanadium(II) complex.

# Summary of the structure of [ONNO]-vanadium complexes

All complexes were characterized by X-ray diffraction studies [28–30]. The aim of this review is not to give a full description of the structure, and below are the conclusions that can be drawn from the solution and solid-state structure determination. Figure 6 presents a summary of the geometry of some [ONNO]-vanadium compounds that were studied.

- The solid-state structures confirmed the formulations and overall geometry given in Figs. 2–5. All compounds share the same features: they are mononuclear complexes, containing an octahedrally coordinated vanadium center surrounded by a tetradentate [ONNO] ligand and additional coligands. Concerning the [ONNO] ligand, in all complexes, the two phenolate rings have a *trans* configuration, as well as coordination of both amino N donor atoms to the metal center.
- Two distinct configurations of the [ONNO] fragment have been observed in the crystal structures (Fig. 6). The configuration of the [ONNO] ligand in the first class of compounds is symmetry-related [the two aromatic rings of the bis(phenolate) framework (without the sidearm)], with the phenolate groups of the [ONNO] framework that fold in toward the pendant (dimethylamino)ethyl side-arm. In contrast, the phenolate groups of the [ONNO]-ligand of the second class of compounds fold back away from the pendant (dimethylamino)ethyl side-arm, with a molecular structure that has two non-symmetry-related phenolate rings. Such a helical distorsion of the tripodal amino N donor atom induces a lower symmetry in the ligand framework. This disymmetric configuration could arise from the presence of an O-ligated anionic ligand (alkoxo, oxo, acac, ...) located in *trans* position in respect to the (dimethylamino)ethyl side-arm N donor atom in these complexes.
- The structure in solution as determined by <sup>1</sup>H, VTP, and NOESY NMR spectroscopic experiments for the diamagnetic complexes [V(V) species], revealed strong coordination of the [ONNO] ligand as a tetradentate ligand, with two symmetry-related phenolate groups in a *trans* configuration.
- When two distinct coligands are present in the octahedral complex, two isomers may be formed, and have been shown to coexist in solution in one case.

Therefore, although the [ONNO] framework was previously qualified as rigid in the sense that it does not decoordinate, it has enough flexibility around the tripodal amino N donor atom to accommodate arrangements that allow the aromatic rings to flip above and under the plane defined by the vanadium center, the tripodal N atom and the two phenolate O atoms.



Fig. 6 Summary of the crystal structures of the [ONNO]-vanadium(V) complexes.

## AMINE-BIS(PHENOLATE)-VANADIUM COMPLEXES, POLYMERIZATION STUDIES

Although vanadium complexes with oxidation number from +3 to +5 are known to catalyze ethylene polymerization, the active species is probably a vanadium(III) complex. Vanadium(II) species are generally considered inactive. To verify this point, we decided to evaluate the catalytic olefin polymerization activity of the members of our family of vanadium complexes supported by the same ancillary ligand [ONNO], and that stabilizes four oxidation states (from +II to +V) of the metal center. These polymerization studies were conducted using EtAlCl<sub>2</sub> as cocatalyst (in preliminary studies, methylalumoxane, MAO, was shown to act as a poor cocatalyst for these systems) [30].

## Ethylene, propylene, and 1-hexene homopolymerization

The catalyst activity of the [ONNO]vanadium(II–V) complexes **1–8** toward ethylene polymerization has been evaluated under the same set of conditions using 10 equiv of  $EtAlCl_2$  under 1 atm of ethylene at 20 °C in toluene. Only the most interesting results are summarized in Table 1, with a comparison with standard vanadium-based catalysts VCl<sub>4</sub> and V(acac)<sub>3</sub> (tested in our hands under the same experimental conditions).

Catalyst	Time (min)	Yield (mg)	Activity <sup>a</sup>	T <sub>m</sub> (°C) <sup>b</sup>	$\frac{M_{\rm w}}{(\rm g/mol \times 10^{-3})^{\rm c}}$	$\frac{M_{\rm n}}{(\rm g/mol \times 10^{-3})^{\rm c}}$	$M_{\rm w}/M_{\rm n}^{\rm c}$
$\overline{V^V O(O^i Pr)[ONNO](1)}$	5*	227	272	134.0	118	44	2.65
$V^{IV}(O^{i}Pr)_{2}[ONNO]$ (4)	3*	237	474	138.7	677	338	2.00
$V^{IV}(Cl)_2[ONNO]$ (5)	15	156	62	139.0	889	438	2.03
VCl <sub>4</sub>	10*	373	22	135.1	152	19	8.13
V <sup>III</sup> (acac)[ONNO] ( <b>6</b> )	3*	218	436	133.4	673	202	3.33
V <sup>III</sup> (Cl)(THF)[ONNO] (7)	15	129	52	135.2	458	204	2.24
V(acac) <sub>3</sub>	10*	141	85	135.8	176	72	2.43
V <sup>II</sup> (tmeda)[ONNO] (8)	15	4	1	n.d.	2259	745	3.03

 Table 1 Ethylene polymerization studies.

Conditions: Catalyst 0.01 mmol in 10 ml of toluene; EtAlCl<sub>2</sub> cocatalyst (10 equiv); ethylene 1 bar; time of polymerization 15 min run except when the solution solidify to give a polymer gel, the asterix (\*) denotes such a reaction.

<sup>a</sup>In kg<sub>PE</sub> mol<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup>.

<sup>b</sup>Determined by DSC.

<sup>c</sup>Determined by SEC in 1,2,4-trichlorobenzene at 140 °C vs. polystyrene standards.

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The vanadium(II) complex V(tmeda)[ONNO] affords only poor yields of PE (which could also be due to a trace amount of dioxygen). We have verified that the absence of activity is not due to the presence of a chelating TMEDA ligand to the metal center, as the activity of the vanadium(III–V) catalysts is only slightly reduced by the presence of 1 equiv of TMEDA, which, as expected, confirms that this reduced oxidation state of the vanadium gives only inactive or less active polymerization catalysts.

Under the same conditions, most of the other [ONNO]-vanadium(III–V) complexes exhibit good activities in ethylene polymerization (ranging from ca. 20 to ca. 500 kg<sub>PE</sub> mol<sup>-1</sup><sub>[V]</sub> h<sup>-1</sup>), and comparable to other vanadium systems described in the literature [10,18,26,34–38], keeping in mind that we used only 10 equiv of EtAlCl<sub>2</sub> cocatalyst (and we did not use a reactivator such as ethyl trichloracetate). Selected examples of the best catalysts are reported in Table 1.

Polymer properties are typical of high-molecular-weight, high-density polyethylenes (HDPEs), with reasonably narrow, unimodal, polydispersity indices ( $M_w/M_n$  ca. 2–3), which suggests that the active species is well defined with the [ONNO] ligand remaining coordinated to the metal during the catalytic process.

Some conclusions can be drawn from these first studies: (i) the V(II) system is inactive; (ii) catalysts with V–Cl or V–N<sub>3</sub> bonds give lower activities, as compared to catalysts that have alkoxide or acac ligands (not presented in the table) [30]; and (iii) the activity and quality of the polyethylenes obtained with the best V(III)–V(V) catalysts are very similar and do not depend on the oxidation states of the metal center (+III to +V). This suggests that these different systems involve a similar catalytic active species that is most probably a [ONNO]-V(III) complex [in the case of the V(IV) and V(V) catalyts, a V(II) active species would result from the reduction of the vanadium center by the aluminum cocatalyst].

Although  $V(acac)_3$  is known to initiate living propene polymerization [39], none of the [ONNO]vanadium complexes could catalyze propene polymerization at 20 °C (propene 4 bars, EtAlCl<sub>2</sub> cocatalyst, V/Al = 1/10). Less surprisingly, we were unable to polymerize 1-hexene with our catalysts, even at high temperatures (70 and 135 °C). The lack of reactivity with such an olefin may result from the stronger steric hindrance of the tetradentate dianionic [ONNO] ligand.

### Ethylene-α-olefin copolymerization

Copolymerization of ethylene with 1-hexene with V(acac)[ONNO] (6) catalyst was conducted at ambient temperature in toluene in the presence of  $EtAlCl_2$  cocatalyst (V/Al = 1/10), under 1–4 bars of ethylene with a ratio catalyst/1-hexene of 1/800, and compare to that of V(acac)<sub>3</sub> (see Table 2). The nature and composition of the polymers were determined by <sup>13</sup>C NMR spectra (at 370 K).

The polymers produced were shown to be poly(ethylene-*co*-hexene)s (EH) typical of EH block copolymers with polyethylene sequences separated by isolated hexene units (no HH dyads are observed). The fact that no HH units are observed is consistent with the previous observation that this catalyst is not active for 1-hexene homo-polymerization. The EH copolymers have low molecular weight (ca.  $33-149 \times 10^3$ ), with a narrow unimodal molecular weight distribution (PDI = 1.70-2.07). The comonomer incorporation in these polymers was found to be relatively modest at 4 bars of ethylene (ca.  $3.6 \mod \%$ ) but decreasing ethylene pressure to 2 bars and 1 bar resulted (logically) in an increase of the 1-hexene content to up to 10.6 % of 1-hexene units.

Similar observations were made for the copolymerization of ethylene and 1-octene (under the same conditions as the one described for 1-hexene). Copolymers with 8–10 % of 1-octene units are produced with good activities.

Catalyst	α-Olefin	Ethylene pressure (bar)	Yield (mg)	Activity <sup>a</sup>	α-Olefin content (mol %) <sup>c</sup>	$\begin{array}{c} M_{\rm w} \\ (g/{\rm mol} \times 10^{-3})^{\rm d} \end{array}$	$\begin{array}{c} M_{\rm n} \\ (g/{\rm mol} \times 10^{-3})^{\rm d} \end{array}$	$M_{\rm w}/M_{\rm n}^{\rm d}$
6 6	1-hexene 1-hexene	2 4	600 702 202	120 140	7.4 3.6	71 149 22	41 72	1.7 2.0
$\frac{0}{V(acac)_3}$	1-hexene	2	838	167	7.5	2882	17	225
6 6	1-octene 1-octene	1 2	358 993	72 199	12.0 8.0	n.d. n.d.	n.d. n.d.	-

**Table 2** Ethylene- $\alpha$ -olefin copolymerization studies.

Conditions: Catalyst (0.01 mmol) in 10 ml of toluene; EtAlCl<sub>2</sub> cocatalyst (10 equiv); ethylene 1–4 bars; 1-alkene 8 mmol; time of polymerization 30 min run.

<sup>a</sup>In kg<sub>PE</sub> mol<sup>-1</sup> h<sup>-1</sup>.

<sup>b</sup>Determined by DSC.

<sup>c</sup>Determined by <sup>13</sup>C NMR (370 K).

<sup>d</sup>Determined by SEC in 1,2,4-trichlorobenzene at 140 °C vs. polystyrene standards.

## Ethylene-cycloolefin copolymerization

The experimental conditions used for the production of cycloolefin copolymers identical to those described above, with norbornene or cyclopentene in place of the  $\alpha$ -olefin, are summarized in Table 3.

**Table 3** Ethylene-cycloolefin copolymerization studies with V(acac)[ONNO].

Cycloolefin	Pressure (bar)	Time (min)	Yield (mg)	Activity <sup>a</sup>	Comonomer content (mol %) <sup>b</sup>
Norbornene	1	30	329	66	29
Norbornene	2	15	730	292	18
Norbornene	4	15	868	347	14
Cyclopentene	1	15	356	142	10
Cyclopentene	2	15*	491	196	6

Conditions: Catalyst (0.01 mmol); toluene 10 ml;  $EtAlCl_2$  cocatalyst (10 equiv); ethylene 1–4 bars; cycloolefin 8 mmol; time of polymerization 15 or 30 min run. <sup>a</sup>In kg<sub>PE</sub> mol<sup>-1</sup> h<sup>-1</sup>.

<sup>b</sup>Comonomer content in mol % determined by <sup>13</sup>C NMR (370 K). <sup>c</sup>Toluene 20 ml.

V(acac)[ONNO] (6) associated with EtAlCl<sub>2</sub> (V/Al = 1/10) was shown to present an interesting catalytic activity for ethylene-norbornene copolymerization (Table 3), with productivities ranging 66–347 kg<sub>copolymer</sub> mol<sup>-1</sup> h<sup>-1</sup> depending on the ethylene pressure being, respectively, 1–4 bars. As revealed by <sup>13</sup>C NMR spectroscopy, the resultant polymer was poly(ethylene-*co*-norbornene) with high norbornene incorporation (14–29 mol %), and with a microstructure that possesses no norbornene repeat units and contains both *meso* and *racemo* alternating ethylene-norbornene sequences as well as isolated norbornene units.

Cyclopentene was copolymerized with ethylene by V(acac)[ONNO]/EtAlCl<sub>2</sub> (V/Al = 1/10) in a similar way, with comparable activities (Table 3) and affording a copolymer that contains 6–10 % of cyclopentene units in the polymer chain.

# CONCLUSION

The amine bis(phenolate) ligand was shown to be a supporting ligand suitable for the synthesis of various vanadium complexes and with stabilization of oxidation states +II to +V of the metal center of these complexes. The [ONNO] ligand provides a rigid and sterically protected environment to the vanadium center that enabled us to use members of the family of [ONNO]-vanadium complexes as ethylene polymerization catalysts in association with an EtAlCl<sub>2</sub> cocatalyst. To our knowledge, this was the first comprehensive study of a catalytic polymerization system with a single ancillary ligand set to stabilize such a broad scale of oxidation states of the metal center. Copolymerization studies show that some of these complexes are efficient catalysts for the production of ethylene- $\alpha$ -olefin and ethylene-cycloolefin copolymers, with good to high incorporation of the comonomer. Current studies are directed toward the modifications of the steric and electronic properties of the ligand, as well as the synthesis of alkyl-vanadium compounds related to mechanistic investigations.

# ACKNOWLEDGMENTS

Financial support for this project was provided by the CNRS. I am indebted to Drs. F. Wolff, R. Choukroun, L. Vendier, and B. Donnadieu for profound and skillful contributions.

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