Synthesis, Structure and 1,3-Butadiene Polymerization Behavior of Vanadium(III) Phosphine Complexes

Giuseppe Leone 1,*, Giorgia Zanchin 1,2, Ivana Pierro 1,3, Anna Sommazzi 4, Alessandra Forni 5 and Giovanni Ricci 1,∗

1 CNR, Istituto per lo Studio delle Macromolecole (ISMAC), via A. Corti 12, I-20133 Milano, Italy; giuseppe.leone@ismac.cnr.it (G.L.); giorgia.zanchin@ismac.cnr.it (G.Z.); ivana.pierro@ismac.cnr.it (I.P.)
2 Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, I-20133 Milano, Italy
3 Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Complesso Monte S. Angelo, Via Cintia, I-80126 Napoli, Italy
4 Versalis S.p.A., Istituto Eni Donegani, via G. Fauser 4, I-28100 Novara, Italy; anna.sommazzi@versalis.eni.com
5 CNR, Istituto di Scienze e Tecnologie Molecolari (ISTM), Università degli Studi di Milano, via C. Golgi 19, I-20133 Milano, Italy; alessandra.forni@istm.cnr.it

* Correspondence: giovanni.ricci@ismac.cnr.it; Tel.: +39-02-2369-9376

Received: 9 November 2017; Accepted: 25 November 2017; Published: 28 November 2017

Abstract: A series of vanadium(III) complexes bearing monodentate tertiary phosphine ligands of the type VCl₃(PR₃Ph₃-n)₂ (n = 0 (1a); n = 1 and R = Me (1b), Et (1c), iPr (1d), Cy (1e); n = 2 and R = Me (1f), Et (1g), Cy (1h)), and VCl₃(PR₃)₂ (R = Cyp (2a), Cy (2b), nPr (2c), tBu (2d)) were synthesized and characterized. In the case of 1c, 1g and 2a single crystals were also obtained and their molecular structures were determined. All the complexes were used, in combination with methylaluminoxane (sMAO) or AlMe₃–free MAO (dMAO), for the polymerization of 1,3-butadiene, exhibiting rather good activity and giving polymers with different microstructure depending on the nature of the phosphine ligand and the type of co-catalyst employed.

Keywords: vanadium phosphine complexes; X-ray structure; 1,3-butadiene polymerization; poly(1,3-butadiene)

1. Introduction

The polymerization of 1,3-butadiene plays an important role in the field of stereospecific polymerization, and it is of great interest for both the academic and industrial world. Lanthanides (e.g., Nd, Pr) and transition metals (e.g., Ti, V, Cr, Fe, Co, Ni) compounds in combination with suitable alkylating agents (e.g., AlEt₃, AlEt₂Cl, MAO) were successfully used for the polymerization of 1,3-butadiene, affording polymers with different structure (i.e., trans-1,4, cis-1,4, isotactic 1,2, syndiotactic 1,2 and mixed cis-1,4/1,2 structure with variable 1,2 content) depending on the catalyst nature [1–3].

In particular, vanadium based catalysts are mainly known for their ability to give highly trans-1,4 poly(1,3-butadiene) [1]. A crystalline, highly stereoregular trans-1,4 poly(1,3-butadiene) (trans-1,4 ≥ 99%) with high molecular weight and melting point of about 130 °C was synthesized with the heterogeneous systems obtained by combining a vanadium chloride (e.g., VCl₃, VCl₄) with an aluminum alkyl (e.g., AlEt₃, AlEt₂Cl) [4]. A highly trans-1,4 poly(1,3-butadiene), but with lower molecular weight and melting point, was also obtained with the soluble catalytic systems VCl₃/THF/AlEt₂Cl [5], V(acac)₃/AlEt₂Cl (acac = acetylacetonate) [6], and V(acac)₃/MAO [7,8]. trans-1,4 Poly(1,3-butadiene)s were also obtained with catalysts based on vanadium(III) complexes.
bearing a bis(imino)pyridyl ligand (i.e., VCl₃[2,6-bis(2,6-iPr₂C₆H₃)NC(Me)]₂(C₅H₅N)); the activity of these systems was, however, rather low [9]. Some vanadium based catalysts were also able to give 1,2 syndiotactic and predominantly cis-1,4 poly(1,3-butadiene)s. V(acac)₃, in combination with AlEt₃, was found to be an efficient catalyst for the synthesis of syndiotactic 1,2 poly(butadiene)s [10]; V(η⁵-C₅H₅)₂Cl and V(η⁵-C₅H₅Me)(PEt₃)₂Cl₂, in combination with MAO, gave polymers with a predominantly cis-1,4 structure (cis content of about 85%) with a quite good activity [11–13]. Essentially cis-1,4 poly(1,3-butadiene)s were also obtained by using some amino-functionalized cyclopentadienyl vanadium(III) complexes (e.g., V[η⁵-C₅H₅CH(CH₂₂)₂NMe₂Cl, V[η⁵-C₅H₅(CH₂₂)₂Ni(CH₂₂)₂Cl] [14].

In recent years, several studies on the use of various transition metal phosphine complexes for the polymerization of 1,3-dienes have been reported [15–24]. Catalysts obtained by combining various phosphine complexes of chromium(II) [15–17] and cobalt(II) [18–20] with MAO were found to be extremely active and selective in the polymerization of 1,3-dienes: highly stereoregular polymers having different structure were obtained depending on the type of metal, the type of ligand and the monomer polymerized [21–24]. As far as we know, up to now, only few examples of vanadium(III) phosphine complexes were reported in the literature [25–31], and only some of them have been used for the polymerization of 1,3-butadiene [31].

In this paper, we report on the synthesis and characterization of several vanadium(III) complexes of the type VCl₃(PR₃)₃ (n = 0 (1a); n = 1 and R = Me (1b), Et (1c), Pr (1d), Cy (1e); n = 2 and R = Me (1f), Et (1g), Cy (1h), and VCl₃(PR₃)₂ (R = cyclopentyl (Cyp, 2a), Cy (2b), Pr (2c), Bu (2d), including single-crystal X-ray structural determination of 1c, 1g and 2a. A preliminary study investigating the catalytic behavior of these novel complexes in the polymerization of 1,3-butadiene is presented.

2. Results and Discussion

The study of phosphine complexes of transition metal halides is an important topic and includes different compounds depending on the metal oxidation state and its position in the periodic table. Toward the left side (i.e., Group 4 and 5) and with oxidation states of III and IV, the phosphine–metal bonds tend to be relatively long, weak and labile, and they have little if any π character [32], even if there are examples for which bond lengths do not correlate with their expected bond orders, as in some titanocenes phosphines adducts [33].

Among the metal–phosphine complexes reported, our interest was in preparing vanadium(III) complexes. Complexes of vanadium(III) with tertiary phosphines were prepared from VCl₃ or VCl₃·3THF. It has been reported that PPh₃ and PCy₃ reacted with VCl₃ to give dimers, i.e., [VCl₃(PR₃)]₂ [29]. Mononuclear complexes with a coordination number of 5 were instead obtained by reacting VCl₃·3THF with PMePh₃, PET₃Ph, and PR₃ (R = Me, Et); with a coordination number of 6 [i.e., VCl₃(P₅Pr₃) and VCl₃(PR₃)₂ (R = Me, Pr)] by reacting VCl₃·3THF with P₅Pr₃, PMe₂Ph and P₅Pr₂Ph [26,28]. With other aliphatic phosphines, only intractable oils were obtained likely due to a reduction-hydrolysis process occurring during the reaction and subsequent workup [32].

In this work, we explore the chemical reactivity of VCl₃·3THF versus tertiary phosphine by extending the spectrum of phosphine ligands: The synthesis of vanadium complexes with PR₃Ph₃-n (n = 0, 1, 2; R = Me, Et, Pr, Cy) and PR₃ (R = Cyp, Cy, Pr, Bu) is reported, including single-crystal X-ray structural determination for VCl₃(PET₃Ph₂) (1c), VCl₃(PET₂Ph₂) (1g) and VCl₃(PCyp₂) (2a).

2.1. Synthesis and Structure of V(III)–Phosphine Complexes

Complexes of type VCl₃(PR₃Ph₃-n)₂ (n = 0; n = 1, R = Me, Et, Cy; n = 2, R = Me) and VCl₃(PR₃)₂ (R = Cyp, Cy) were obtained in good yield as microcrystalline solids by addition of the phosphine to a VCl₃·3THF suspension in toluene (P/V = 4:1 mole ratio). Single crystals, suitable for X-ray structure determination, were obtained for 1b, whose structure was previously reported [25,27,30], 1c and 2a from cold pentane. In contrast, the reaction in toluene with phosphine of type PR₃Ph₃-n (n = 2, R = Et, Bu, Cy) and PR₃ (R = Pr, Bu) gave an oily product, difficult to recover. Dusty solids were instead successfully obtained by performing the reaction in THF and adding the ligand dropwise;
single crystals, suitable for X-ray structure determination, were obtained only for \(1g\). Due to their low stability in air, all crystals required low temperature to minimize crystal decay during X-ray data collection (130 K for \(1b\) [30], and 150 K for \(1g\) and 100 K for \(2a\), according to their different stability). A list of selected bond distances and angles for \(1b\) [30], \(1c\), \(1g\) and \(2a\) as obtained by X-ray investigation is reported in Table 1, while a view of the molecular structures of \(1c\), \(1g\) and \(2a\) is reported in Figure 1. DFT gas-phase geometry optimizations, starting from the experimental structures, have been performed on the four complexes in order to discern the effect of crystal packing, if any, on the experimental geometries. Two exchange-correlation functionals have been used to assess the reliability of the theoretical investigation: M06 [34], due to its specific parametrization on organometallic complexes, and B3LYP [35–37], by far the most used functional for geometry optimizations. The results are reported as well in Table 1. At a glance, M06 showed much better performance with respect to B3LYP as far as bond lengths are concerned, while bond angles are in all cases quite similar.

<table>
<thead>
<tr>
<th>Bond Lengths and Angle</th>
<th>VCl(_3)(PMePh(_2))(_2) (1b)</th>
<th>VCl(_3)(PEtPh(_2))(_2) (1c)</th>
<th>VCl(_3)(PET(_2)Ph)(_2) (1g)</th>
<th>VCl(_3)(PCyp(_3))(_2) (2a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V–Cl</td>
<td>2.2287(8)</td>
<td>2.2408(6)</td>
<td>2.246(10)</td>
<td>2.247(10)</td>
</tr>
<tr>
<td></td>
<td>2.243</td>
<td>2.243</td>
<td>2.245</td>
<td>2.251</td>
</tr>
<tr>
<td></td>
<td>2.255</td>
<td>2.255</td>
<td>2.258</td>
<td>2.261</td>
</tr>
<tr>
<td>V–P</td>
<td>2.5280(6)</td>
<td>2.5465(6)</td>
<td>2.5196(11)</td>
<td>2.5696(10)</td>
</tr>
<tr>
<td></td>
<td>2.537</td>
<td>2.551</td>
<td>2.549</td>
<td>2.587</td>
</tr>
<tr>
<td></td>
<td>2.607</td>
<td>2.617</td>
<td>2.613</td>
<td>2.660</td>
</tr>
<tr>
<td>P–C(_{ar})</td>
<td>1.820(2)</td>
<td>1.8251(19)</td>
<td>1.813(4)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.825</td>
<td>1.826</td>
<td>1.828</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.840</td>
<td>1.841</td>
<td>1.841</td>
<td>-</td>
</tr>
<tr>
<td>P–C(_{aliph})</td>
<td>1.822(2)</td>
<td>1.8332(19)</td>
<td>1.828(4)</td>
<td>1.847(3)</td>
</tr>
<tr>
<td></td>
<td>1.828</td>
<td>1.844</td>
<td>1.842</td>
<td>1.850</td>
</tr>
<tr>
<td></td>
<td>1.843</td>
<td>1.861</td>
<td>1.860</td>
<td>1.869</td>
</tr>
<tr>
<td>Cl–V–Cl</td>
<td>119.98(3)</td>
<td>119.99(2)</td>
<td>114.6(2)</td>
<td>120.00(4)</td>
</tr>
<tr>
<td></td>
<td>120.00</td>
<td>120.00</td>
<td>119.98</td>
<td>120.00</td>
</tr>
<tr>
<td></td>
<td>120.00</td>
<td>120.00</td>
<td>119.98</td>
<td>120.00</td>
</tr>
<tr>
<td>P–V–P</td>
<td>169.02(2)</td>
<td>177.87(2)</td>
<td>167.24(4)</td>
<td>170.48(3)</td>
</tr>
<tr>
<td></td>
<td>174.74</td>
<td>177.79</td>
<td>174.06</td>
<td>174.66</td>
</tr>
<tr>
<td></td>
<td>175.06</td>
<td>177.78</td>
<td>174.25</td>
<td>174.77</td>
</tr>
<tr>
<td>C(<em>{ar})–P–C(</em>{ar})</td>
<td>103.73(10)</td>
<td>103.85(8)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>103.64</td>
<td>104.39</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>103.74</td>
<td>104.29</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C(<em>{ar})–P–C(</em>{aliph})</td>
<td>105.20(11)</td>
<td>105.42(9)</td>
<td>105.1(2)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>104.03</td>
<td>104.31</td>
<td>104.20</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>104.09</td>
<td>104.53</td>
<td>104.17</td>
<td>-</td>
</tr>
<tr>
<td>C(<em>{aliph})–P–C(</em>{aliph})</td>
<td>-</td>
<td>-</td>
<td>103.7(2)</td>
<td>105.5(2)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>102.79</td>
<td>104.09</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>102.87</td>
<td>104.99</td>
</tr>
</tbody>
</table>

* Each reported value was obtained as weighted average on all the corresponding parameters present in the structure.

More precisely, both functionals provide similar trends in the geometrical parameters along the series of complexes, generally in agreement with the experimental ones. M06, however, reproduces bond lengths within 0.015 Å, with the only exception of V–P distances which show a maximum discrepancy of 0.029 Å. B3LYP overestimates bond lengths by up to 0.032 Å, excepted for the V–P bonds for which the maximum deviation grows up to 0.093 Å. In the following we therefore rely
only on the M06 optimized geometry. The complexes adopt slightly distorted trigonal-bipyramidal geometry, where the main distortion comes from the deviation (by up to 13°) of the P–V–P angles from 180°. As previously discussed [30], such a deviation is mainly due to crystal packing forces (essentially C–H···Cl [38], C–H···π and π–π intermolecular interactions, the latter two arising in structures where phenylphosphines are present), as denoted by the more regular conformation as obtained by gas-phase calculations, which provide a maximum 6° deviation from a P–V–P straight angle. As a general observation, the V–P bond lengths, ranging on average from 2.520(1) to 2.570(1) Å (2.537 to 2.587 Å from UM06 calculations) in the compounds here investigated, appear to be much longer than the Mt–P (Mt = metal) ones as found in tetrahedral MtCl₂(PR₃Ph_3-n)₂ complexes, suggesting weaker bonds with scarce or null π-character for the vanadium complexes. For example, in the extended series of CoCl₂(PR₃Ph_3-n)₂ complexes previously reported by some of us [18–20,39], the longest Co–P bond distance was found to be 2.437(6) Å for the more sterically hindered CoCl₂(PCy₃)₂ complex [19], well below the V–P shortest distance here reported. Along the series of 1b, 1c, 1g and 2a complexes, the trend in the V–P and, in a lesser extent, the V–Cl average bond lengths generally follows the combined effect of the bulkiness of the phosphine ligand and its π-character. In fact, they increase with either increasing the hindrance of the phosphine and/or decreasing the π-character of the phosphine substituents. For example, going from 1b to 1c, the bulkier ethyl compared to the methyl group implies an increase in the average V–P distance, ∆r(V–P) = 0.018(1) Å (0.014 Å from theory). Comparing 1b, 1c and 1g with 2a, we observe a definite increase ∆r(V–P) = 0.042(1), 0.023(1) and 0.050(1) Å, respectively (0.050, 0.036 and 0.038 Å from theory), due to both the large hindrance of the cyclopentyl group and the absence of any π-electron group in the phosphine. Interestingly, replacement of one phenyl by an ethyl group (compare 1c with 1g), implying conflicting effects (reduced hindrance together with reduced π-character of the phosphine) leads to V–P shortening, ∆r(V–P) = −0.027(1), suggesting a dominance of the steric over the electronic effect. However, this result should be also ascribed to crystal packing forces because gas-phase calculations provide only minor contraction, ∆r(V–P) = −0.002 Å.

**Figure 1.** Molecular structures of VCl₃(PEtPh_2)₂ (1c) (left), VCl₃(PEt₂Ph)₂ (1g) (center) and VCl₃(PCyp₃)₂ (2a) (right) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity.

Considering the P–C bond lengths involving the aromatic carbon atoms, P–C_ar, they are approximately constant within the experimental error, while those involving the aliphatic carbon atoms, P–C_aliph, follow the same trend as observed for the V–P bonds, though with a lower variability. Comparing 1b, 1c and 1g with 2a, we observe in fact an increase ∆r(P–C_aliph) = 0.025(3), 0.014(3) and 0.019(4) Å, respectively (0.022, 0.006 and 0.008 Å from theory). The C–P–C bond angles are essentially unvaried in the four structures, with the only exception of the C_aliph–P–C_aliph angle, which as expected undergoes a small but non negligible increase, equal to 1.8(2)°, well reproduced by calculations (1.3°), going from 1g to 2a.
2.2. Polymerization of 1,3-Butadiene

The polymerization of 1,3-butadiene with all the vanadium(III) phosphine complexes synthesized, in the presence of white solid MAO [dMAO, prepared by removing toluene and AlMe₃ from commercially available MAO (sMAO)] or sMAO as co-catalyst, was examined. The polymerization runs were carried out in toluene at room temperature. The most significant results are summarized in Table 2.

All the vanadium complexes, in combination with dMAO, were active in the polymerization of 1,3-butadiene, giving low to good polymer yields, ranging from 13 to 57% (Table 2, entry 17 and 1, respectively), within the first 2 h of polymerization. By extending the polymerization runs up to 24 h, it was possible to reach complete monomer consumption (Table 2, entry 2), meaning that the catalysts are not deactivated with time, as it occurs in the polymerization of ethylene where high concentration of reoxidant (typically Cl₃CCOOEt or chlorinated hydrocarbons) is required to keep the catalyst active [30,40,41]. This can be ascribed to the higher nucleophilicity of 1,3-butadiene with respect to a simple olefin, but mainly to the higher stability of the vanadium–π-allyl bond compared to the vanadium–alkyl bond of the intermediate species involved in the polymerization of 1,3-butadiene and ethylene, respectively [42].

The results in Table 2 are presented as a function of the phosphine donor ability [as measured by the electronic parameter $v_{CO}$ based on the carbonyl stretching frequencies in Ni(CO)$_3$L complexes (L = phosphine ligand)] and steric properties (measured by cone angle, $\theta$) as defined by Tolman [43,44], to highlight the influence of the ligand (i.e., the type of substituents on the phosphorous atoms) on the catalytic activity and selectivity. A general increasing of the activity by decreasing the $\sigma$-donor character (increasing $\pi$-acceptor character) of the phosphine ligand was observed, irrespective of the ligand steric hindrance. Electron-withdrawing groups on the ligand framework seem to enhance catalytic performance. Complexes with aryl phosphine exhibited higher activity than those bearing alkyl phosphines, as shown in Figure 2 (catalyst using PCyp$_3$ makes an exception to this trend). The P$^t$Bu$_3$ (the strongest $\sigma$-donor) yields the least active system, confirming the strong influence of the phosphine basicity on the catalytic activity.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Phosphine</th>
<th>$v_{CO}$ (cm$^{-1}$)</th>
<th>$\theta$ (°)</th>
<th>Yield (%)</th>
<th>$N$ (h$^{-1}$)</th>
<th>cis:trans:1,2</th>
<th>$M_w$ (×10$^3$)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a/dMAO</td>
<td>PPh$_3$</td>
<td>2068.9</td>
<td>145</td>
<td>57</td>
<td>739</td>
<td>33:31:36</td>
<td>275</td>
<td>1.9</td>
</tr>
<tr>
<td>2</td>
<td>1a/dMAO</td>
<td>PPh$_3$</td>
<td>2068.9</td>
<td>145</td>
<td>100</td>
<td>123</td>
<td>30:34:36</td>
<td>290</td>
<td>1.6</td>
</tr>
<tr>
<td>3</td>
<td>1a/sMAO</td>
<td>PPh$_3$</td>
<td>2068.9</td>
<td>145</td>
<td>51</td>
<td>63</td>
<td>65:19:16</td>
<td>177</td>
<td>4.2</td>
</tr>
<tr>
<td>4</td>
<td>1b/dMAO</td>
<td>PMePh$_2$</td>
<td>2067.0</td>
<td>136</td>
<td>46</td>
<td>593</td>
<td>29:37:34</td>
<td>270</td>
<td>2.1</td>
</tr>
<tr>
<td>5</td>
<td>1b/sMAO</td>
<td>PMePh$_2$</td>
<td>2067.0</td>
<td>136</td>
<td>7</td>
<td>93</td>
<td>69:17:14</td>
<td>164</td>
<td>1.9</td>
</tr>
<tr>
<td>6</td>
<td>1c/dMAO</td>
<td>PEtPh$_2$</td>
<td>2066.7</td>
<td>140</td>
<td>42</td>
<td>360</td>
<td>30:38:32</td>
<td>83</td>
<td>2.1</td>
</tr>
<tr>
<td>7</td>
<td>1d/dMAO</td>
<td>PiPrPh$_2$</td>
<td>2065.7</td>
<td>150</td>
<td>50</td>
<td>648</td>
<td>28:33:39</td>
<td>112</td>
<td>3.5</td>
</tr>
<tr>
<td>8</td>
<td>1d/sMAO</td>
<td>PiPrPh$_2$</td>
<td>2065.7</td>
<td>150</td>
<td>17</td>
<td>222</td>
<td>66:18:16</td>
<td>102</td>
<td>2.6</td>
</tr>
<tr>
<td>9</td>
<td>1e/dMAO</td>
<td>PCyPh$_2$</td>
<td>2064.8</td>
<td>153</td>
<td>43</td>
<td>46</td>
<td>67:15:18</td>
<td>100</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 2. Polymerization of 1,3-butadiene with the phosphine V(III) complexes.$^a$

---

$^a$ Conditions: Toluene, 20°C. Entry 9 (catalyst using PCyp$_3$ makes an exception to this trend).
Table 2. Cont.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>N (mol 1,3-butadiene/mmol V/h)</th>
<th>Mw (g/mol)</th>
<th>Mw/Mn</th>
<th>θ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 f</td>
<td>dMAO PMe</td>
<td>2065.3</td>
<td>122</td>
<td>43</td>
<td>556</td>
</tr>
<tr>
<td>12 g</td>
<td>dMAO PEt</td>
<td>2063.7</td>
<td>136</td>
<td>37</td>
<td>480</td>
</tr>
<tr>
<td>13 h</td>
<td>dMAO PCy</td>
<td>2060.9</td>
<td>159</td>
<td>25</td>
<td>324</td>
</tr>
<tr>
<td>14 a</td>
<td>dMAO PCyp</td>
<td>2056.4</td>
<td>170</td>
<td>21</td>
<td>269</td>
</tr>
<tr>
<td>15 b</td>
<td>dMAO PnPr</td>
<td>2059.1</td>
<td>132</td>
<td>26</td>
<td>333</td>
</tr>
<tr>
<td>16 c</td>
<td>dMAO PnBu</td>
<td>2056.1</td>
<td>182</td>
<td>13</td>
<td>167</td>
</tr>
</tbody>
</table>

*polymerization conditions: 1,3-butadiene, 2 mL (1.4 g); solvent, toluene (16 mL); V(III)-complex, 10 µmol; Al/V, 1000; time, 2 h (* 24 h in runs 2, 3 and 10); *b* measure of the electron-donating properties of phosphine ligands, as reported by Tolman [43,44]; *c* phosphine cone angle, as reported by Tolman [43,44]; *d* N = moles of 1,3-butadiene polymerized per mol of vanadium per hour; *e* determined by $^1$H and $^{13}$C NMR; *f* determined by SEC.

The type of phosphine ligand was also found to have some effect, though not very pronounced, on the polymerization selectivity, as suggested by the microstructure of the resulting poly(1,3-butadiene)s determined by $^1$H and $^{13}$C NMR (Table 2 and Figures S1–S4). Generally, all the vanadium complexes, in combination with dMAO, gave polymers with a mixed cis-1,4/trans-1,4/1,2 structure, the 1,4 and 1,2 units being randomly distributed along the polymer chain, as indicated by the fact that fractionation of the polymers with boiling solvents always gives polymeric fractions having practically the same structure of the pristine polymers; however, the 1,4 content seems to be higher for poly(1,3-butadiene)s obtained with catalysts based on vanadium complexes bearing more hindered phosphine ligands ($θ ≥ 150°$).

The influence of the type of alkylating agent (dMAO versus sMAO) on the catalytic activity and selectivity was also investigated: under the same polymerization conditions, catalysts using sMAO as co-catalyst resulted to be less active, giving polymers with higher 1,4 content, the cis-1,4 units being predominant (Table 2, entry 4 vs. 5, entry 2 vs. 3, entry 7 vs. 8, and entry 9 vs. 10).

A spread of the weight-average molecular weights, depending on the complex used, ranging from rather low ($M_w = 75,000$ g/mol, entry 11) to significantly higher ($M_w = 296,000$ g/mol, entry 16), was observed. The molecular weight distributions ($M_w/M_n$) were fairly narrow, although tending to a certain broadening in some cases.

![Figure 2](image-url)
concerned, at the same polymerization conditions (i.e., monomer and catalyst concentration, solvent and temperature polymerization), vanadium systems are considerably less active than chromium (e.g., CrCl$_2$(dmpe)$_2$/MAO) [15] and cobalt (e.g., CoCl$_2$(P$^3$PrPh$_2$)$_2$/MAO) [18] ones, while they are comparable to those titanium-based (e.g., TiCl$_2$(dmpe)$_2$/MAO) [39] and clearly more active than the iron-based ones [39] just because the latter are practically inactive; (ii) concerning instead the catalytic selectivity, vanadium systems are characterized by the lowest stereospecificity since they essentially provide poly(1,3-butadiene)s with mixed 1,4/1,2 structure, while titanium based systems allow to obtain predominantly cis-1,4 poly(1,3-butadiene)s (≥80%) [39] and cobalt based systems can give highly cis-1,4 or highly 1,2 syndiotactic poly(1,3-butadiene)s, depending on the type of phosphine ligand on the cobalt atom [18–20,39].

3. Materials and Methods

3.1. General Procedures and Materials

Manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk-line techniques. Nitrogen was purified by passage over columns of CaCl$_2$, molecular sieves and BTS catalysts. THF (Aldrich, St. Louis, MO, USA, ≥99.9%) was refluxed over Na/benzophenone alloy for eight h and then distilled and stored over molecular sieves. Toluene (Aldrich, >99.5%) was refluxed over Na for 8 h and then distilled and stored over molecular sieves. Pentane (Aldrich, >99%) was refluxed over Na/K alloy for eight h and then distilled and stored over molecular sieves. Tri-normal-propylphosphine (P$_3$nPr$_3$) (Strem, Newburyport, MA, USA, 95%), tricyclopentylphosphine (PCyp$_3$) (Strem, >97%), tricyclohexylphosphine (PCy$_3$) (Strem, 97%), methylidyophosphine (PMMePh$_2$) (Strem, 99%), dimethylphenylphosphine (PMe$_2$Ph) (Strem, 99%), ethyldiphosphine (PEtPh$_2$) (Aldrich, 98%), diethylphosphine (PMe$_2$Ph) (Aldrich, 96%), di-tert-butylmethylphosphine (P$_2$Bu$_2$Me) (Strem, >98%), iso-propyldiphosphine (P$^3$PrPh$_2$) (Aldrich, 97%), cyclohexyldiphenylphosphine (PCyPh$_2$) (Strem, 99%), dicyclohexylphenylphosphine (PCy$_2$Ph) (Aldrich, 95%), triphenylphosphine (PPh$_3$) (Aldrich, ≥95%), tri-tert-butylphosphine (P$_2$Bu$_3$) (Aldrich, 95%), MAO (Aldrich, 10 wt % solution in toluene) and VCl$_3$(THF)$_3$ (Aldrich) were used as received. Solid MAO (dMAO) was prepared by removing toluene and unreacted free trimethylaluminum under vacuum from commercially available MAO solution (sMAO). The resulting white powder was heated further to 50 °C under vacuum overnight. 1,3-Butadiene (Air Liquide, Milano, Italy, >99.5% pure) was evaporated from the container prior to each run, dried by passing through a column packed with molecular sieves and condensed into the reactor which had been precooled to −20 °C. Deuterated solvent for NMR measurements (C$_4$D$_2$Cl$_4$) (Aldrich, >99.5% atom D), was used as received. For the Elemental Analysis a Perkin Elmer CHN Analyzer 2400 Series II (Perkin Elmer, Milano, Italy) was used.

3.2. Synthesis of the V(III)–Phosphine Complexes

3.2.1. Trichlorobis(triphenylphosphine)vanadium(III) [VCl$_3$(PPh$_3$)$_2$, 1a]

PPh$_3$ (2.08 g, 10.6 mmol) was added to a suspension of VCl$_3$(THF)$_3$ (0.99 g, 2.65 mmol, P/V = 4:1) in toluene (15 mL) at room temperature. The solution turned rapidly brown, it was kept under stirring overnight, and then concentrated to half of its volume. Pentane (50 mL) was added dropwise and a light brown precipitate was rapidly formed. The suspension was filtered and the solid residue on the filter washed with pentane (3 × 20 mL), then dried under vacuum to give 1a as lilac powder (Yield, 83%). Attempts to obtain crystals suitable for the molecular structure determination failed. FTIR (cm$^{-1}$): 3054 (vw), 1589 (w), 1482 (w), 1436 (m), 1158 (m), 1119 (m), 1093 (m), 991 (m), 748 (mw), 723 (s), 692 (s), 533 (s), 496 (mw). Anal. Calcd. for C$_{36}$H$_{30}$Cl$_3$P$_2$V: C, 63.41; H, 4.43; Cl, 15.60; P, 9.08; V, 7.47. Found: C, 63.30; H, 4.50; Cl, 15.50; P, 9.0; V, 7.60.
3.2.2. Trichlorobis(methylidiphenylphosphine)vanadium(III) [VCl$_3$(PMePh)$_2$, 1b]

1b was synthesized in the same way as described for 1a using PMePh$_2$ (2.19 g, 11 mmol) and VCl$_3$(THF)$_3$ (1.02 g, 2.73 mmol, P/V = 4:1), and it was obtained as red-purple powder (Yield, 90%). The solid was then extracted continuously with boiling pentane. Crystals of 1b were formed directly on the bottom of the Schlenk tube during the extraction, and further crops of crystals were obtained by cooling the supernatant pentane solution at −30 ºC [30]. FTIR (cm$^{-1}$): 3053 (w), 2927 (vs), 1587 (vw), 1484 (w), 1436 (m), 1144 (m), 1120 (m), 1098 (m), 1028 (w), 997 (m), 908 (w), 734 (s), 539 (m), 509 (s), 481 (m). Anal. Calcd. for C$_{28}$H$_{26}$Cl$_3$P$_2$V: C, 55.99; H, 4.70; Cl, 19.07; P, 11.10; V, 9.13. Found: C, 56.20; H, 4.60; Cl, 19.20; P, 11.10; V, 9.20.

3.2.3. Trichlorobis(ethylidiphenylphosphine)vanadium(III) [VCl$_3$(PEtPh)$_2$, 1c]

1c was synthesized in the same way as described for 1a using PEtPh$_2$ (2.9 g, 13.7 mmol) and VCl$_3$(THF)$_3$ (1.28 g, 3.42 mmol), and it was obtained as lilac powder (Yield, 91%). The solid was then extracted continuously with boiling pentane. Crystals of 1c were formed directly on the bottom of the Schlenk tube during the extraction, and further crops of crystals were obtained by cooling the supernatant pentane solution at −30 ºC. FTIR (cm$^{-1}$): 3054 (vw), 2927 (vs), 1587 (vw), 1484 (w), 1436 (m), 1144 (m), 1120 (m), 1098 (m), 1028 (w), 997 (m), 908 (w), 734 (s), 539 (m), 509 (s), 481 (m). Anal. Calcd. for C$_{28}$H$_{30}$Cl$_3$P$_2$V: C, 57.41; H, 5.16; Cl, 18.16; P, 10.58; V, 8.70. Found: C, 57.40; H, 5.10; Cl, 18.20; P, 10.07; V, 8.60.

3.2.4. Trichlorobis(iso-propyldiphenylphosphine)vanadium(III) [VCl$_3$(P$i$PrPh)$_2$, 1d]

1d was synthesized in the same way as described for 1a using $i$PrPh$_2$ (2.0 g, 8.76 mmol) and VCl$_3$(THF)$_3$ (0.82 g, 2.19 mmol), and it was obtained as pink powder (Yield, 91%). FTIR (cm$^{-1}$): 3054 (vw), 2963 (w), 1587 (w), 1482 (w), 1460 (w), 1437 (m), 1153 (m), 1120 (m), 1060 (m), 992 (m), 879 (w), 740 (s), 691 (vs), 538 (m), 521 (s), 490 (m), 460 (m). Anal. Calcd. for C$_{30}$H$_{32}$Cl$_3$P$_2$V: C, 58.70; H, 5.58. Found: C, 58.64; H, 5.54.

3.2.5. Trichlorobis(cyclohexylidiphenylphosphine)vanadium(III) [VCl$_3$(PCyPh)$_2$, 1e]

1e was synthesized in the same way as described for 1a using PCyPh$_2$ (2.4 g, 9.0 mmol) and VCl$_3$(THF)$_3$ (0.86 g, 2.3 mmol), and it was obtained as light blue powder (Yield, 56%). Attempts to obtain crystals useful to determine the structure of the complex failed. FTIR (cm$^{-1}$): 3055 (vw), 2930 (m), 2875 (w), 1589 (w), 1483 (w), 1437 (m), 1152 (m), 1118 (s), 1097 (m), 1028 (w), 999 (s), 917 (w), 888 (w), 851 (w), 822 (w), 741 (s), 724 (s), 690 (vs), 554 (s), 529 (vs), 499 (m), 486 (m), 463 (w). Anal. Calcd. for C$_{32}$H$_{42}$Cl$_3$P$_2$V: C, 62.31; H, 6.10; Cl, 15.33; P, 8.93; V, 7.34. Found: C, 62.40; H, 6.30; Cl, 15.50; P, 9.0; V, 7.20.

3.2.6. Trichlorobis(dimethylphenylphosphine)vanadium(III) [VCl$_3$(PMe$_2$Ph)$_2$, 1f]

1f was synthesized in the same way as described for 1a using PMe$_2$Ph (1.06 g, 7.7 mmol) and VCl$_3$(THF)$_3$ (0.72 g, 1.92 mmol), and it was obtained as pale pink powder (Yield, 87%). Attempts to obtain crystals useful to determine the structure of the complex failed. FTIR (cm$^{-1}$): 3053 (w), 1435 (mw), 1140 (mw), 997 (mw), 951 (m), 840 (mw), 745 (vs), 693 (vs), 485 (m). Anal. Calcd. for C$_{16}$H$_{22}$Cl$_3$P$_2$V: C, 44.50; H, 5.11. Found: C, 44.50; H, 5.20.

3.2.7. Trichlorobis(diethylphenylphosphine)vanadium(III) [VCl$_3$(PEt$_2$Ph)$_2$, 1g]

PEt$_2$Ph (1.0 g, 6.1 mmol) was added dropwise to a suspension of VCl$_3$(THF)$_3$ (0.85 g, 2.26 mmol, P/V = 2:6:1) in THF (25 mL) at room temperature. The solution turned from dark red to green rapidly and was kept under stirring overnight, then concentrated to half of its volume. Pentane (50 mL) was added dropwise and a beige oily product formed. The mixture was kept under stirring overnight. The solvent was discarded, leaving the oily product behind, washed with pentane (3 × 40 mL) and...
finally dried in vacuo. A successive addition of a large excess of pentane, and leaving at −30 °C for 3 h produced green chunks of 1g (Yield, 85%). Crystals of 1g were formed directly on the bottom of the Schlenk tube during the extraction, and further crops of crystals were obtained by cooling the supernatant pentane solution at −30 °C. FTIR (cm⁻¹): 3054 (vw), 2938 (w), 1589 (w), 1485 (w), 1455 (m), 1438 (s), 1398 (m), 1268 (w), 1248 (w), 1130 (vs), 1107 (vs), 1072 (s), 1049 (s), 1020 (s), 1001 (vs), 934 (w), 898 (w), 762 (s), 746 (s), 725 (s), 678 (s), 515 (s), 477 (m). Anal. Calcd. for C_{20}H_{30}Cl_{3}P_{2}V: C, 49.05; H, 6.17. Found: C, 49.17; H, 6.23.

3.2.8. Trichlorobis(dicyclohexylphenylphosphine)vanadium(III) [VCl_{3}(PCy_{2}Ph)_{2}, 1h]

1h was synthesized in the same way as described for 1g using PCy_{2}Ph (1.0 g, 3.65 mmol) and VCl_{3}(THF)_{3} (0.55 g, 1.48 mmol), and it was obtained as light green powder (Yield, 76%). Attempts to obtain crystals useful to determine the structure of the complex failed. FTIR (cm⁻¹): 3054 (w), 2924 (vs), 2851 (s), 1588 (w), 1439 (s), 1328 (w), 1299 (w), 1271 (w), 1177 (w), 1125 (m), 1069 (w), 1003 (s), 905 (m), 850 (m), 747 (s), 696 (s), 508 (m), 487 (m). Anal. Calcd. for C_{36}H_{54}Cl_{3}P_{2}V: C, 61.24; H, 7.71. Found: C, 61.19; H, 7.68.

3.2.9. Trichlorobis(tricyclopentylphosphine)vanadium(III) [VCl_{3}(PCyp_{3})_{2}, 2a]

2a was synthesized in the same way as described for 1a using PCyp_{3} (2.9 g, 13.7 mmol) and VCl_{3}(THF)_{3} (0.92 g, 2.44 mmol), and it was obtained as a pink powder (Yield, 65%). The solid was then extracted continuously with boiling pentane. Crystals of 2a were formed directly on the bottom of the Schlenk tube during the extraction, and further crops of crystals were obtained by cooling the supernatant pentane solution at −30 °C. FTIR (cm⁻¹): 2949 (vs), 2866 (vs), 1448 (m), 1299 (mw), 1261 (mw), 1231 (mw), 1126 (m), 1053 (m), 1028 (m), 994 (vs), 907 (mw), 806 (s), 508 (m), 487 (m). Anal. Calcd. for C_{30}H_{54}Cl_{3}P_{2}V: C, 56.83; H, 8.59; Cl, 16.78; P, 9.77; V, 8.03. Found: C, 56.90; H, 8.70; Cl, 16.70; P, 9.80; V, 8.0.

3.2.10. Trichlorobis(tricyclohexylphosphine)vanadium(III) [VCl_{3}(PCy_{3})_{2}, 2b]

2b was synthesized in the same way as described for 1a using PCy_{3} (2.47 g, 8.82 mmol) and VCl_{3}(THF)_{3} (0.83 g, 2.20 mmol), and it was obtained as a light grey powder (Yield, 55%). Attempts to obtain crystals useful to determine the structure of the complex failed. FTIR (cm⁻¹): 3277 (vw), 2927 (vs), 2851 (vs), 1446 (s), 1262 (w), 1107 (m), 1053 (m), 1028 (m), 994 (vs), 907 (mw), 806 (s), 508 (m), 487 (m). Anal. Calcd. for C_{36}H_{66}Cl_{3}P_{2}V: C, 60.21; H, 9.26; Cl, 14.81; P, 8.63; V, 7.09. Found: C, 60.30; H, 9.20; Cl, 14.70; P, 8.80; V, 8.0.

3.2.11. Trichlorobis(tri-normal-propylphosphine)vanadium(III) [VCl_{3}(P^{n}Pr_{3})_{2}, 2c]

2c was synthesized in the same way as described above for 1g using the ligand P^{n}Pr_{3} (1.08 g, 6.72 mmol) and VCl_{3}(THF)_{3} (1.0 g, 2.20 mmol), and it was obtained as a beige powder (Yield, 35%). Attempts to obtain crystals useful to determine the structure of the complex failed. FTIR (cm⁻¹): 2093 (mw), 2933 (mw), 2874 (mw), 2903 (mw), 1461 (m), 1403 (m), 1380 (mw), 1243 (vw), 1071 (m), 997 (m), 916 (m), 733 (mw). Anal. Calcd. for C_{18}H_{42}Cl_{3}P_{2}V: C, 45.25; H, 8.86. Found: C, 45.10; H, 8.78.

3.2.12. Trichlorobis(tri-tert-butylphosphine)vanadium(III) [VCl_{3}(P^{t}Bu_{3})_{2}, 2d]

2d was synthesized in the same way as described above for 1g using the ligand P^{t}Bu_{3} (1.74 g, 8.64 mmol) and VCl_{3}(THF)_{3} (0.46 g, 2.16 mmol), and it was obtained as gray/brown powder (Yield, 31%). FTIR (cm⁻¹): 3029 (vw), 2971 (w), 1592 (w), 1472 (m), 1402 (w), 1379 (w), 1261 (w), 1175 (m), 1097 (w), 998 (s), 934 (w), 871 (m), 807 (m), 732 (w), 672 (m), 618 (w), 584 (m), 493 (m), 474 (m). Anal. Calcd. for C_{23}H_{54}Cl_{3}P_{2}V: C, 51.30; H, 9.69; Cl, 18.93; P, 11.02; V, 9.07. Found: C, 51.50; H, 9.50; Cl, 19.10; P, 11.20; V, 9.30.
3.3. X-ray Crystallographic Studies

The intensity data were collected on a Bruker Smart Apex CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction was made using SAINT programs; absorption corrections based on multiscan were obtained by SADABS [45]. The structures were solved by SHELXS-97 [46], and refined on F² by full-matrix least-squares using SHELXL-14 [47]. All the non-hydrogen atoms were refined anisotropically, hydrogen atoms were included as ‘riding’ and not refined. The isotropic thermal parameters of H atoms were fixed at 1.2 (1.5 for methyl groups) times the equivalent thermal parameter of the atoms to which they are bonded. Crystal data and results of the refinement: (1c) air-sensitive orange prism 0.50 × 0.20 × 0.20 mm, Mr = 585.75, monoclinic, space group P2₁/c, a = 8.3234(12) Å, b = 9.7489(14) Å, c = 34.500(5) Å, β = 93.804(2)°, V = 2793.3(7) Å³, Z = 4, T = 130(2) K, μ = 0.773 mm⁻¹. 37,054 measured reflections, 5141 independent reflections, 4377 reflections with I > 2σ(I), 2.36 < 2θ < 50.91°, Rint = 0.0468. Refinement on 5141 reflections, 309 parameters. Final R = 0.0261, wR = 0.0564 for data with F² > 2σ(F²), S = 1.036, (Δ/σ)max = 0.001, ∆ρmax = 0.286, ∆ρmin = −0.249 eÅ⁻³; (1g) air-sensitive light blue tablet 0.25 × 0.12 × 0.10 mm, Mr = 489.67, orthorhombic, space group P2₁2₁2₁, a = 11.9609(5) Å, b = 13.8664(5) Å, c = 13.9617(5) Å, V = 2315.61(15) Å³, Z = 4, T = 150(2) K, μ = 0.916 mm⁻¹. 46,227 measured reflections, 6991 independent reflections, 6547 reflections with I > 2σ(I), 4.49 < 2θ < 60.84°, Rint = 0.0364. Refinement on 6991 reflections, 239 parameters. Final R = 0.0485, wR = 0.1459 for data with F² > 2σ(F²), S = 1.076, (Δ/σ)max = 0.001, ∆ρmax = 1.109, ∆ρmin = −1.955 eÅ⁻³; (2a) air-sensitive red tablet 0.50 × 0.17 × 0.15 mm, Mr = 633.96, triclinic, space group P-1, a = 9.9362(15) Å, b = 11.7793(18) Å, c = 14.673(2) Å, α = 83.712(2)°, β = 89.645(2)°, γ = 66.242(2)°, V = 1561.0(4) Å³, Z = 2, T = 100(2) K, μ = 0.696 mm⁻¹. 16,969 measured reflections, 4488 independent reflections, 3859 reflections with I > 2σ(I), 2.80 < 2θ < 46.60°, Rint = 0.0395. Refinement on 4488 reflections, 325 parameters. Final R = 0.0385, wR = 0.0911 for data with F² > 2σ(F²), S = 1.066, (Δ/σ)max = 0.002, ∆ρmax = 0.606, ∆ρmin = −0.940 eÅ⁻³. Table S1 contains cartesian coordinates of the modelled compounds at their UM06/6-311G(d) optimized geometry; while CCDC 1583626–1583628 contain supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.4. Computational Details

Geometry optimization of the isolated, gas phase vanadium(III) complexes were performed with the 6-311g(d) basis set by the Gaussian16 program package [48], starting from the respective X-ray molecular structures. For comparative purposes, two exchange-correlation functionals have been used: the M06 functional [34], due to its specific parametrization on organometallic complexes, and the B3LYP functional [35–37], the most used functional for geometry optimizations. According to previous magnetic measurements on 1b [25], complexes were modeled in their triplet state through the unrestricted formalism.

3.5. Polymerization of 1,3-Butadiene

Polymerizations were carried out in a 25 mL round-bottomed Schlenk flask. Prior to starting polymerization, the reactor was heated to 110 °C under vacuum for one h and backfilled with nitrogen. 1,3-Butadiene was condensed into the Schlenk flask kept at −20 °C, then toluene was added and the solution was brought to the desired polymerization temperature. The aluminum alkyl and a toluene solution (2 mg/mL) of the vanadium complex were then added in that order. Polymerization was stopped with methanol containing a small amount of hydrochloric acid. The polymer obtained was then coagulated by adding 40 mL of a methanol solution containing 4% of Irganox® 1076 antioxidant (BASF, Ludwigshafen am Rhein, Germany), repeatedly washed with fresh methanol and finally dried in vacuum at room temperature to constant weight.
3.6. Polymer Characterization

For all the mentioned catalysts the FTIR spectrum was collected. Attenuated total reflectance (ATR)-Fourier transform infrared spectroscopy (FTIR) spectra were recorded at room temperature in the 600–4000 cm\(^{-1}\) range with a resolution of 4 cm\(^{-1}\) using a Perkin Elmer Spectrum Two spectrometer (Perkin Elmer, Milano, Italy.). NMR spectra were recorded on a Bruker NMR advance 400 Spectrometer (Bruker Italia Srl, Milano, Italy) operating at 400 MHz (1H) and 100.58 MHz (\(^{13}\)C) working in the PFT mode at 103 °C. NMR samples were prepared dissolving from 60 to 80 mg of polymer in about three mL of C\(_2\)D\(_2\)Cl\(_4\) in 10 mm probes and referred to hexamethyldisiloxane (HMDS), as internal standard. The relaxation delay was 16 s. The molecular weight average (\(M_w\)) and the molecular weight distribution (\(M_w/M_n\)) were obtained by a high temperature Waters GPCV2000 size exclusion chromatography (SEC) system equipped with a refractometer detector. The experimental conditions consisted of three PL Gel Olexis columns, ortho-dichlorobenzene (DCB) as the mobile phase, 0.8 mL/min flow rate, and 145 °C temperature. The calibration of the SEC system was constructed using eighteen narrow \(M_w/M_n\) PS standards with molar weights ranging from 162 to 5.6 × 10\(^6\) g/mol. For SEC analysis, about 12 mg of polymer was dissolved in five mL of DCB with 0.05% of BHT as antioxidant.

4. Conclusions

A series of V(III) complexes with aryl and alkyl phosphines were synthesized and characterized, including single crystal X-ray molecular structure determination of VCl\(_3\)(PEtPh\(_2\))\(_2\), VCl\(_3\)(PEt\(_2\)Ph)\(_2\) and VCl\(_3\)(PCyp\(_3\))\(_2\). The complexes were then successfully used, in combination with various aluminoxanes, for the polymerization of 1,3-butadiene. In general, we obtained polymers having different microstructures, depending on the phosphine ligand and the Al-based activator. Catalysts based on vanadium complexes with more hindered ligands gave poly(1,3-butadiene) with higher 1,4 (cis + trans) content (≥80 mol %); catalysts with sMAO as co-catalyst were found to give higher cis-1,4 content (≥65 mol %). The type of ligand and co-catalyst were also found to have some influence on the catalyst activity. In general catalysts based on complexes with aryl phosphines exhibited higher activity than those bearing alkyl phosphines; catalysts using dMAO instead of sMAO as co-catalyst resulted to be much more active, allowing to reach complete monomer conversion, thus indicating that vanadium catalysts in case of conjugated diolefins polymerization are not subject to deactivation and do not need the use of a reoxidant, as it happens in case of monoolefins.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/7/12/369/s1.
Table S1: Cartesian coordinates of the modeled compounds at their UM06/6-311G(d) optimized geometry, Figure S1: \(^1\)H NMR spectrum of poly(1,3-butadiene) (Table 2, entry 4), Figure S2: \(^{13}\)C NMR spectrum of poly(1,3-butadiene) (Table 2, entry 4), Figure S3: \(^1\)H NMR spectrum of poly(1,3-butadiene) (Table 2, entry 14), Figure S4: \(^{13}\)C NMR spectrum of poly(1,3-butadiene) (Table 2, entry 14).

Author Contributions: G.L. performed the experiments, analyzed the data, and contributed to write the paper. G.Z. performed the experiments and a part of them were reproduced by I.P. and A.S.; A.F. determined the X-ray molecular structures of the complexes, performed the quantum-mechanical calculations and contributed to write the paper. G.R. was the principal investigator, conceived and designed the experiments, analyzed the data and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References
6. Porri, L.; Carbonaro, A.; Ciampelli, F. Copolymerization of 1,3-butadiene and 1,3-pentadiene with homogeneous Al (C2H5)2Cl-vanadium compounds catalyst systems. I. Preparation and properties of the copolymers. Makromol. Chem. 1963, 61, 90–103. [CrossRef]


38. Aakeröy, C.B.; Evans, T.A.; Seddon, K.R.; P. [CrossRef]


© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).