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Easily accessible, hydrocarbon-soluble, crystalline, anhydrous lanthanide (Nd, La, and Y) phosphates†

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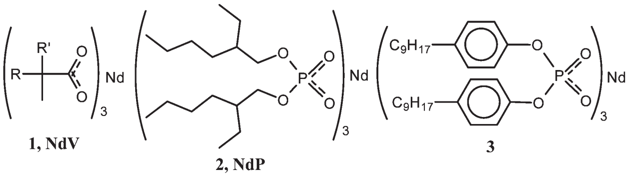
Nd, La and Y triphosphates were prepared *via* the reaction of potassium ionol ethyl phosphate with the corresponding lanthanide nitrates or chlorides in water. According to the X-ray diffraction data, the recrystallised reaction products were dimers. The products did not contain water, were readily soluble in hydrocarbon solvents and demonstrated promising catalytic properties in the polymerisation of butadiene and DL-dilactide.

Introduction

Lanthanide derivatives have found wide use in organic synthesis and homogeneous catalysis.[1] The use of lanthanide compounds as catalysts of butadiene 1,4-*cis*-polymerisation is their most important application in homogeneous catalysis.[2] Usually, these processes utilise neodymium carboxylate and phosphate salts with lipophilic anions, such as neodymium versatate, **NdV**, **1**[3] (a mixture of isomers of different α,α-disubstituted decanoic acids that is also referred to as neodymium neodecanoate), neodymium tris[bis(2-ethylhexyl)phosphate], **NdP**, **2**[4,5] and neodymium tris[bis(*para*-nonylphenyl)phosphate] **3**[6] (see Scheme 1).

The use of lipophilic anions makes neodymium derivatives soluble in hydrocarbons in which the process of polymerisation is most efficient.[2] However, due to the high electronic and steric unsaturation of the neodymium ions in compounds such as **NdV** and **NdP**, these neodymium derivatives form oligomers of uncertain composition due to neodymium coordination to the oxygen atoms of the neighbouring molecules.[7,8] Therefore, the "solutions" of **NdV** and **NdP** represent non-homogeneous and viscous gels and the reactivity of neodymium in such derivatives is substantially reduced and critically depends on the method of salt preparation. Obviously, the presence of different Nd species in the gels of NdV and NdP not only complicates the application of these compounds as catalysts and reduces the potential process parameters (broadens the polydispersity of the polymer and reduces the activity of the catalyst)[7] but also complicates the study of Nd-catalysed polymerisation, as it is impossible to reliably identify the individual intermediates.



1, NdV **2, NdP** **3**

Scheme 1 The structures of neodymium carboxylate and phosphate salts with lipophilic anions.

There are several approaches that can be used to suppress the oligomerisation of neodymium salts in solution. Kwag succeeded in preparing the adduct of neodymium tris-neodecanoate with an additional equivalent of the carboxylic acid and showed that the activity of this monomeric complex is almost one order of magnitude higher than the activity of standard neodymium tris-neodecanoate.[7] Yet another possible method for suppressing the oligomerisation of neodymium carboxylates and phosphates is the use of bulky and more structurally rigid anions. Previously, this strategy was utilised by Anwander in the preparation of neodymium derivatives based on *ortho*-substituted benzoic acids.[9] Anwander was able to not only isolate individual neodymium carboxylates but also to unambiguously characterise several products obtained by alkylation with trimethylaluminium. These works as well as the investigation by Evans,[10] who isolated intermediate chlorine-containing lanthanide compounds and studied the role of chlorine in

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neodymium catalysis, provided considerable progress in the understanding of neodymium catalysis of diene polymerisation. Unfortunately, due to the difficulty in obtaining the benzoic acids used and the moderate performance of the resulting neodymium complex catalysts, no further studies of the Anwander-type catalysts derived from the substituted benzoic acids were performed.

During the current work, we demonstrated that the oligomerisation of lanthanide salts in solutions can be completely prevented by the use of bulky and structurally rigid ionol-containing phosphate anions and that this approach is beneficial for the catalytic properties of the compounds. The corresponding phosphoric acid can be easily prepared from cheap and readily available reagents such as ionol, ethanol and $POCl_3$.

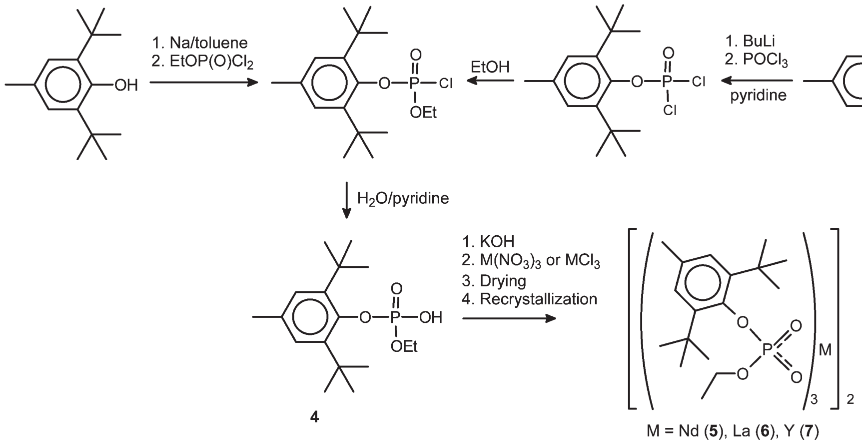
Results and discussion

We undertook the synthesis of lanthanide (Nd, La, and Y) derivatives of previously unknown but readily accessible ionol ethyl phosphoric acid **4**. This acid, as we demonstrated, can be easily obtained in acceptable yields by the hydrolysis of the corresponding acid chloride, which is in turn prepared by either the reaction of sodium ionolate with $EtOP(O)Cl_2$ or by successive reactions of $POCl_3$ with lithium ionolate and ethanol (Scheme 2).

The reaction of the potassium salt of acid **4** with neodymium nitrate in water at a reactant ratio of 3 : 1 gives a high yield of crude neodymium tris-phosphate **5** formed as a precipitate, which can be purified by recrystallisation from hexane. Lanthanum and yttrium tris-phosphates **6** and **7**, respectively, can be prepared by a similar method to the neodymium derivative. According to the X-ray diffraction data, complexes **5–7** are dimers.

The crystallographic data, data collection and refinement parameters for **5**, **6** and **7** are given in the Experimental section (Table 3). The bimetallic phosphate complexes **5** and **6** are isostructural (Fig. 1). The metal core of **5** and the main geometrical parameters for **5** and **6** are shown in Fig. 1. The central atoms have CN = 7 and possess an irregular coordination polyhedron. The lengths of the non-bridging M–O bonds vary within 2.3259(17)–2.4305(16) Å for **5** and 2.386(3)–2.488(2) Å for **6**, while the M–O(14) bridging bonds are significantly longer (2.7425(17) Å for **5** and 2.793(2) Å for **6**). In general, the La–O distances are approximately 2.5% longer than the corresponding Nd–O bonds. In both complexes, the metal atoms are linked by four phosphate ligands. Two of the metal atoms are tridentate chelating bridges (with central P(1) atoms) and two are bidentate bridges (with central P(2) atoms). Additionally, the metal centres bear terminal chelating ligands with central P(3) atoms. In the ligands, all the phosphorous atoms are tetrahedral with O–P–O angles lying within 101.8(1)–115.9(2)°. The P–O distances clearly split into three non-overlapping ranges: $P–O_{Met}$ (1.487(3)–1.5106(16) Å); $P–O_{Et}$ (1.557(3)–1.576(3) Å) and $P–O_{Ar}$ (1.580(3)–1.603(3) Å). The significant shortening of the $P–O_{Met}$ bonds (in comparison with the single $P–O_{Et}$ and $P–O_{Ar}$ bonds) is a result of their partial double-bond character.

The structure of the bimetallic complex **7** is presented in Fig. 2. Both yttrium atoms possess a strongly distorted octahedral coordination environment. The metal atoms are linked by four bidentate bridging ligands (with central P(1), P(2), P(3) and P(4) atoms). Additionally, the metal centres bear terminal chelating ligands containing central P(5) and P(6) atoms. The Y–O bonds formed by the terminal ligands (2.306(3)–2.317(3) Å) are noticeably longer than those formed by the bridging phosphate esters (2.223(3)–2.267(3) Å). All four bridging ligands exhibit significant asymmetry. Thus, the P(*n*)–O(*n*3)–Y angles are approximately 35° less than the corresponding P(*n*)–O(*n*4)–Y angles (*n* = 1–4). As expected, the $P–O_{Ar}$ and $P–O_{Et}$ distances are ~0.06 Å longer than the $P–O_{Met}$ bond lengths. The basal planes of the oppositely lying terminal ligands (specifically, P(5), O(53), O(54) and P(6), O(63), O(64)) are almost perpendicular. The angle between these ligands is 89.1(2)°. In contrast, the same planes in the structures of **5** and **6** (namely P(3A), O(33A), O(34A) and P(3), O(33), O(34)) are parallel due to the symmetry of these molecules.



Scheme 2 Synthesis of ionol ethyl phosphoric acid **4** and phosphates **5–7** of this acid.

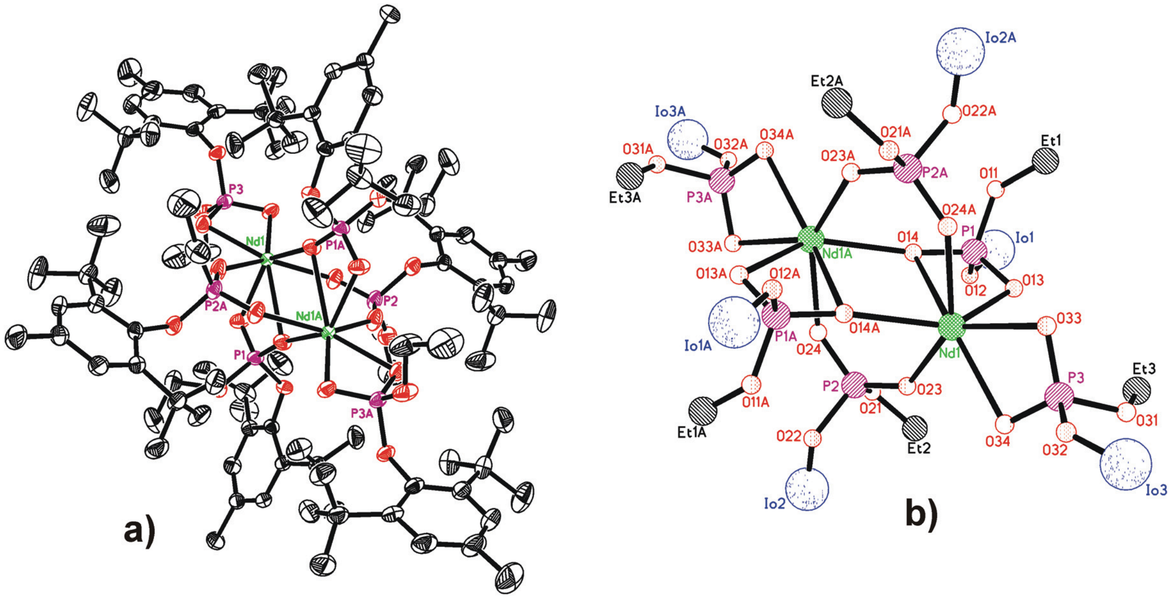


Fig. 1 Molecular structures of **5** and **6**. (a) Full structure, displacement ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for clarity. (b) Metal core in the structures of **5** and **6**. For clarity, the ethyl and 2,6-di-*t*-butyl-4-methylphenoxy groups are drawn as circles and denoted as Et and Io, respectively. Selected bond distances (Å) and angles (°) in **5**: Nd(1)⋯Nd(1A) 4.0172(6), Nd(1)–O(13) 2.3796(16), Nd(1)–O(14)$_{\text{bridge}}$ 2.7425(17), Nd(1)–O(14A) 2.3860(16), Nd(1)–O(23) 2.3698(16), Nd(1)–O(24A) 2.3259(17), Nd(1)–O(33) 2.4215(16), Nd(1)–O(34) 2.4305(16), P(1)–O(11)$_{\text{Et}}$ 1.5601(18), P(1)–O(12)$_{\text{Ar}}$ 1.5862(17), P(1)–O(13)$_{\text{Met}}$ 1.4985(18), P(1)–O(14)$_{\text{Met}}$ 1.5106(16), P(2)–O(21)$_{\text{Et}}$ 1.5641(19), P(2)–O(22)$_{\text{Ar}}$ 1.5961(18), P(2)–O(23)$_{\text{Met}}$ 1.4966(18), P(2)–O(24)$_{\text{Met}}$ 1.4910(18), P(3)–O(31)$_{\text{Et}}$ 1.5679(18), P(3)–O(32)$_{\text{Ar}}$ 1.5765(16), P(3)–O(33)$_{\text{Met}}$ 1.5028(17), P(3)–O(34)$_{\text{Met}}$ 1.5050(17), P(1)–O(13)–Nd(1) 104.96(9), P(1)–O(14)–Nd(1) 89.62(8), P(1)–O(14)–Nd(1A) 167.44(10), Nd(1)–O(14)–Nd(1A) 102.91(5), P(2)–O(23)–Nd(1) 138.34(10), P(2)–O(24)–Nd(1A) 142.59(10), P(3)–O(33)–Nd(1) 96.66(8), P(3)–O(34)–Nd(1) 96.23(8). Selected bond distances (Å) and angles (°) in **6**: La(1)⋯La(1A) 4.1139(8), La(1)–O(13) 2.442(3), La(1)–O(14)$_{\text{bridge}}$ 2.793(2), La(1)–O(14A) 2.448(3), La(1)–O(23) 2.424(2), La(1)–O(24A) 2.386(3), La(1)–O(33) 2.479(3), La(1)–O(34) 2.488(2), P(1)–O(11)$_{\text{Et}}$ 1.557(3), P(1)–O(12)$_{\text{Ar}}$ 1.584(3), P(1)–O(13)$_{\text{Met}}$ 1.496(3), P(1)–O(14)$_{\text{Met}}$ 1.508(3), P(2)–O(21)$_{\text{Et}}$ 1.570(3), P(2)–O(22)$_{\text{Ar}}$ 1.603(3), P(2)–O(23)$_{\text{Met}}$ 1.501(3), P(2)–O(24)$_{\text{Met}}$ 1.487(3), P(3)–O(31)$_{\text{Et}}$ 1.576(3), P(3)–O(32)$_{\text{Ar}}$ 1.580(3), P(3)–O(33)$_{\text{Met}}$ 1.496(3), P(3)–O(34)$_{\text{Met}}$ 1.504(3), P(1)–O(13)–La(1) 105.04(13), P(1)–O(14)–La(1) 90.14(12), P(1)–O(14)–La(1A) 166.63(16), La(1)–O(14)–La(1A) 103.23(8), P(2)–O(23)–La(1) 138.79(15), P(2)–O(24)–La(1A) 143.11(16), P(3)–O(33)–La(1) 97.22(12), P(3)–O(34)–La(1) 96.62(12).

Owing to their good solubility in non-polar solvents, for example in chloroform-d_1 and benzene-d_6, tris-phosphates can be studied by NMR. In the ^{31}P NMR ($CDCl_3$) spectrum of yttrium derivative **7**, the signals of the terminal (−1.55 ppm) and bridging phosphates (−14.42 ppm) are clearly distinguished. In lanthanum derivative **6**, bridging phosphates differ in their X-ray diffraction data but still produce only one signal in the ^{31}P NMR spectrum (−14.50 ppm) due to the similar nature and fast chemical exchange on the NMR time scale. Terminal phosphates are responsible for a separate signal (−3.95 ppm). Unfortunately, the paramagnetism of the Nd(III) ion precludes recording informative NMR spectra of complex **5**. Nevertheless, the identity of structures **5** and **6** in the crystalline state and the similarity of the chemical properties of lanthanum and neodymium suggest that in solution, the structures of these compounds are also identical. Thus, the dimeric phosphate complexes in unpolar and non-coordinating solvents have the same dimeric structures as they have in the crystalline state.

Only a few structures of homoleptic lanthanide complexes with phosphate diesters are currently known, specifically, complexes containing La, Ce, Pr, Nd, Sm and Eu.[11] Only the simplest symmetric dimethyl and diethyl phosphate ligands $(RO)_2PO_2$ were used in these investigations and all of the reported structures were polymeric in the crystal. In contrast, the structures of **5–7** presented herein are dimeric due to the steric requirements of the bulky 2,6-di-*t*-butyl-4-methylphenoxy groups. No short intermolecular contacts were found in the structures of **5–7**. Thus, by using bulky and structurally rigid phosphate ligands, we succeeded in completely preventing the oligomerisation of phosphates **5–7**. As a result, the compounds we obtained were not only readily soluble in hydrocarbon solvents but also formed non-viscous solutions.

To elucidate the effect of oligomerisation on the catalytic properties of neodymium phosphate **5**, we studied its catalytic properties in the polymerisation of butadiene and compared the results with the properties of the commercial neodymium 2-ethylhexyl phosphate **2** and neodymium tris[bis(*para*-nonylphenyl) phosphate] **3**, which represents the derivative of the lipophilic but not a very bulky bis(*para*-nonylphenyl) phosphoric acid. The catalyst is usually prepared by the reaction of the neodymium derivative with an organoaluminium reagent (AlR_3, $AlHR_2$) and chlorinating reagent (Et_2AlCl, $Et_3Al_2Cl_3$).[2] According to the mechanism of the catalysis proposed by Kwag,[7] the catalytic site represents a compound of the type XNdRCl (X = phosphate or carboxylate, R = alkyl). We prepared the catalyst *via* alkylation of phosphate **5** with diisobutylaluminium hydride in the presence of butadiene followed by the addition of ethylaluminium sesquichloride ($Et_3Al_2Cl_3$). Table 1 summarises the experimental data obtained. Surprisingly, it

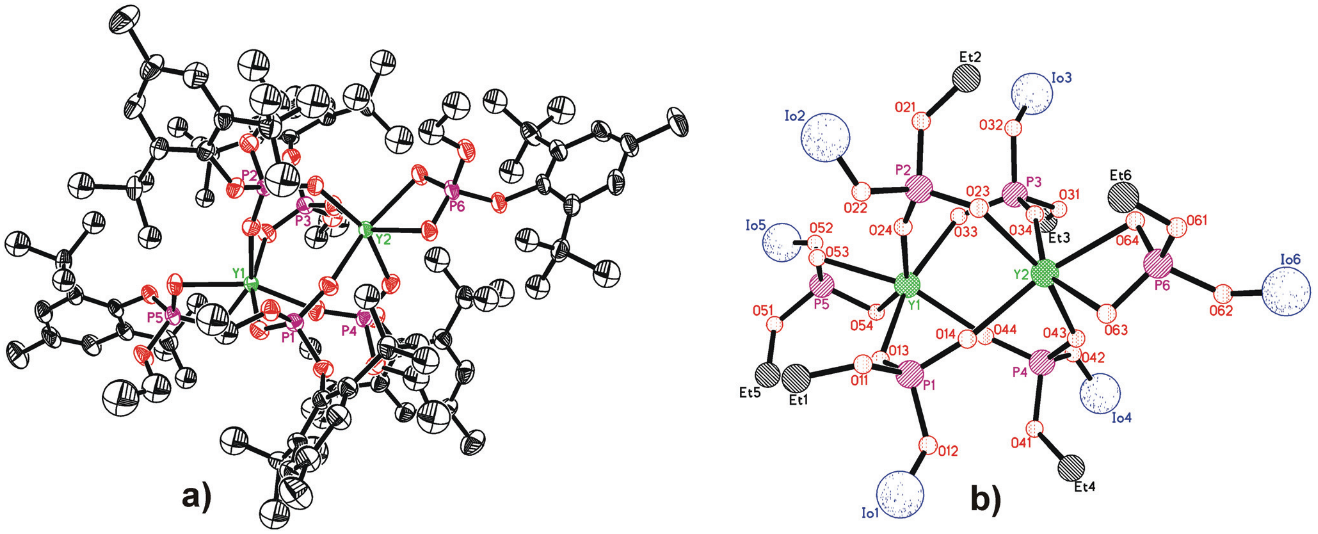


Fig. 2 Molecular structure of **7**. (a) Full structure, displacement ellipsoids are drawn at a 30% probability level. Hydrogen atoms are omitted for clarity. (b) Metal core in the structure of **7**. For clarity, the ethyl and 2,6-di-*t*-butyl-4-methylphenoxy groups are drawn as circles and denoted as Et and Io, respectively. Selected bond distances (Å) and angles (°) in **7**: Y(1)–O(13) 2.267(3), Y(2)–O(14) 2.237(3), Y(1)–O(24) 2.236(3), Y(2)–O(23) 2.252(3), Y(1)–O(33) 2.236(3), Y(2)–O(34) 2.223(3), Y(1)–O(44) 2.226(3), Y(2)–O(43) 2.237(3), Y(1)–O(53) 2.317(3), Y(2)–O(63) 2.306(3), Y(1)–O(54) 2.315(3), Y(2)–O(64) 2.308(3), P(1)–O(11)$_{\text{Et}}$ 1.566(4), P(1)–O(13)$_{\text{Met}}$ 1.489(4), P(1)–O(12)$_{\text{Ar}}$ 1.595(4), P(1)–O(14)$_{\text{Met}}$ 1.489(4), P(2)–O(21)$_{\text{Et}}$ 1.551(4), P(2)–O(23)$_{\text{Met}}$ 1.499(3), P(2)–O(22)$_{\text{Ar}}$ 1.582(4), P(2)–O(24)$_{\text{Met}}$ 1.488(4), P(3)–O(31)$_{\text{Et}}$ 1.557(4), P(3)–O(33)$_{\text{Met}}$ 1.498(4), P(3)–O(32)$_{\text{Ar}}$ 1.581(4), P(3)–O(34)$_{\text{Met}}$ 1.486(4), P(4)–O(41)$_{\text{Et}}$ 1.570(4), P(4)–O(43)$_{\text{Met}}$ 1.491(4), P(4)–O(42)$_{\text{Ar}}$ 1.578(4), P(4)–O(44)$_{\text{Met}}$ 1.492(4), P(5)–O(51)$_{\text{Et}}$ 1.551(4), P(5)–O(53)$_{\text{Met}}$ 1.493(4), P(5)–O(52)$_{\text{Ar}}$ 1.565(4), P(5)–O(54)$_{\text{Met}}$ 1.502(4), P(6)–O(61)$_{\text{Et}}$ 1.561(4), P(6)–O(63)$_{\text{Met}}$ 1.501(4), P(6)–O(62)$_{\text{Ar}}$ 1.557(4), P(6)–O(64)$_{\text{Met}}$ 1.506(4), Y(1)⋯Y(2) 4.0770(7), P(1)–O(13)–Y(1) 122.9(2), P(1)–O(14)–Y(2) 164.8(2), P(2)–O(23)–Y(2) 123.66(19), P(2)–O(24)–Y(1) 164.1(2), P(3)–O(33)–Y(1) 127.3(2), P(3)–O(34)–Y(2) 159.8(2), P(4)–O(43)–Y(2) 127.4(2), P(4)–O(44)–Y(1) 161.0(2), P(5)–O(53)–Y(1) 95.96(17), P(5)–O(54)–Y(1) 95.79(17), P(6)–O(63)–Y(2) 95.74(16), P(6)–O(64)–Y(2) 95.49(17).

Table 1 Butadiene polymerisation by complexes **5**, **2** and **3** at 50 °C

Run	Complex	Nd : AlH^{i}Bu$_2$: Cl	Yield	1,4-*cis*, %	1,4-*trans*, %	1,2-, %	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	Ref.
1	**5**	1 : 15 : 2.5	>99	97.7	2.2	0.1	237.9	479.6	2.01	This work
2	**3**	—	90	96.0	2.7					6
3	**2**	—	100	95.7	a	a	185	325	1.76	5
4	**2***	1 : 15 : 2.5	>99	95.1	4.1	0.8	120.2	160.9	1.34	This work

Conditions: hexane, V_{total} = 20 ml, [butadiene] = 1.5 M, [Nd] = 1.5 × 10^{-4} M, [i-Bu$_2$AlH] = 4.5 × 10^{-3} M, [Cl] = 3.75 × 10^{-4} M, reaction time = 2 h.

was found that the presence of bulky *ortho*-substituents in phosphate **5** does not reduce the catalytic activity of this compound but rather increases it compared with **3** (*cf.* runs 1 and 2). Moreover, the prevention of the oligomerisation in **5** results in a markedly different microstructure of the polymers obtained using **5** rather than oligomeric **2** and **3**. For complexes **2** and **3**, only a 95–96% content of the 1,4-*cis*-component can be achieved but the use of **5** under the same conditions allows one to increase this value to nearly 98%. Note that a similar increase in the content of the 1,4-*cis*-component was observed by Kwag during his study of monomeric neodymium tris-neodecanoate.[7] Thus, we demonstrate that the suppression of oligomerisation in a solution of neodymium phosphate **5** has a pronounced influence on its catalytic performance in 1,4-*cis*-butadiene polymerisation by both enhancing the catalyst activity and increasing the degree of process stereoregularity.

The application of organic neodymium phosphates, usually neodymium 2-ethylhexyl phosphate **2**, is not limited to the stereoregular polymerisation of conjugated dienes. It has been shown that catalytic systems based on organic neodymium phosphates can be used in the polymerisation of acetylene,[12] acrylonitrile,[13] methyl methacrylate,[14] and styrene,[15] in the copolymerisation of carbon dioxide and epichlorohydrin[16] and in the copolymerisation of isoprene and epichlorohydrin.[17] Because of our interest in the polymerisation of dilactide, we investigated the effect of the non-oligomeric nature of phosphates **5–7** on their ability to initiate dilactide polymerisation. The ability to use neodymium 2-ethylhexyl phosphate **2** in this process has previously been demonstrated[18] and the application of some carboxylates also reported.[19] In both cases, the results were moderate and a reasonable conversion was achieved only at temperatures above 100 °C. In our opinion, this rather low activity of the studied phosphates and

Table 2 Results of the polymerisation of D,L-dilactide catalysed by complexes **5**, **6**, **7**, and **2**

Run	Complex	T, °C	Conversion (NBR), %[a]	$M_{n,\ NMR} \times 10^{-3}$ [b]	$M_{n,\ calc} \times 10^{-3}$ [c]	$M_n \times 10^{-3}$ (GPC)	M_w/M_n (GPC)
1	**6**	80	>99	6.9	7.2	8.2	1.3
2	**5**	80	>99	8.7	7.2	8.3	1.2
3	**2**	80	85	5.4	6.1	6.6	1.1
4	**7**	80	75	6.1	5.4	6.5	1.1
5	**6**	60	>99	4.6	7.2	7.0	1.1
6	**5**	60	75	4.1	5.4	4.7	1.2

Conditions: $n_{D,L} : n_{complex} : n_{Et_3Al} : n_{iPrOH} = 100 : 1 : 2 : 1$, where $n_{D,L}$, $n_{complex}$, n_{Et_3Al}, n_{iPrOH} are the initial amounts of the dilactide, the complex, Et_3Al and *i*PrOH, respectively.[a] The conversion was determined by integrating the signals of the methine protons of the dilactide (5.04 ppm in $CDCl_3$) and polylactide (5.12–5.26 ppm in $CDCl_3$). [b] $M_{n,\ NMR}$ was determined by integrating the signals of the methine protons of the polylactide and the methine protons of the polylactide terminal units (4.19 ppm in $CDCl_3$). [c] $M_{n,\ calc} = 144 \times$ dilactide amount/Et_3Al amount × dilactide conversion.

carboxylates is due exclusively to oligomerisation of the neodymium salts. Indeed, other more sophisticated neodymium derivatives described recently can polymerise dilactide under mild conditions at high rates.[20]

We studied the polymerisation of dilactide catalysed by the "phosphate"/[Et_3Al]/[iPrOH] = 1/2/1 system, where the "phosphate" was represented by derivatives **5–7**, which were synthesised in this work, or by the commercial neodymium 2-ethylhexyl phosphate **2**. The catalyst was prepared by alkylation of phosphates **2** and **5–7** with two equivalents of Et_3Al, and the addition of 1 equivalent of isopropanol initiated the polymerization of the dilactide.[19] Complexes **5** and **6** proved to be quite active catalysts of polylactide synthesis, whereas the activities of **7** and **2** were markedly lower, see Table 2. Indeed, at 80 °C, **5** and **6** provide an almost quantitative conversion of the dilactide, while in the presence of **7** and **2**, the reaction goes only to approximately two-thirds completion. Interestingly, a decrease in the reaction temperature to 60 °C results in considerable differentiation of the activities of the lanthanum and neodymium phosphates. While the conversion on the lanthanum complex **6** is almost quantitative, in the presence of the neodymium complex **5**, it is only 65%. Thus, we demonstrated that for lactide polymerisation, the non-associated individual catalyst **5** has a higher catalytic activity than the oligomeric neodymium 2-ethylhexyl phosphate **2**. An interesting finding is that the lanthanum phosphate **6** is a markedly more active catalyst than the neodymium analogue **5**, which substantially surpasses the yttrium complex **7**.

Conclusion

Thus, in this work we synthesised Nd, La and Y triphosphates based on ionol ethyl phosphoric acid. These compounds are remarkable for two reasons: first, they can be easily prepared in water but do not contain water and second, they are individual non-oligomerised compounds of a definite composition. These features not only provide good solubility of the triphosphates in hydrocarbon solvents but the compounds also qualitatively surpass the conventional oligomeric organic phosphates in their catalytic properties, such as in the polymerisation of butadiene and DL-dilactide. It is likely that the lanthanide triphosphates based on ionol ethyl phosphoric acid and their related compounds could be successfully utilised for many applications that require soluble lanthanide derivatives of a definite composition.

Experimental

Synthesis

In the synthesis of 2,6-di-*tert*-butyl-4-methylphenyl ethyl phosphoric acid, commercial ionol (Merk) and $EtOPOCl_2$, prepared by a known procedure,[21] were used. The lanthanide triphosphates were prepared from $Nd(NO_3)_3 \times 6H_2O$, $LaCl_3 \times 7H_2O$ and $YCl_3 \times 6H_2O$ (Reakhim). The hexane used in the catalyst synthesis and polymerisation was dried by reflux over sodium wire. D,L-Dilactide (Aldrich) was recrystallised from toluene and dried *in vacuo*. Isopropanol (Lab-Scan, 99.8%) was dried and distilled from CaH_2. Toluene (Sigma-Aldrich, 99.8%) was dried and distilled from sodium. NMR spectra were recorded on a Bruker Avance 400 instrument in $CDCl_3$ at 30 °C. The microstructures of polybutadiene were measured by IR spectroscopy (IFS-66v/s Bruker) according to published data.[22] Gel permeation chromatography was performed on a high-pressure chromatograph equipped with a Styrogel HR 5E, HR 4E system of columns using a Rheodyne injector with a 200 µl loop and a Waters 2410 refractometer. THF was used as the eluent.

Synthesis of 2,6-di-*tert*-butyl-4-methylphenyl-ethyl phosphoric acid (4)

Method A: A 1-litre flask with a reflux condenser was charged with ionol (110 g, 0.5 mol), sodium (15 g, 0.65 mol) and toluene (200 ml). The mixture was stirred at reflux until the hydrogen evolution ceased (~5 h). Then, $EtOPOCl_2$ (89.62 g, 0.55 mol) was added with stirring and ice water cooling. After 1 h, the mixture was filtered to remove excess sodium, the filtrate was concentrated *in vacuo*, dissolved in pyridine (200 ml) and water (20 ml) was then added. The mixture was stirred for 3 h and concentrated *in vacuo*, HCl was added to a highly acidic pH (~50 ml) and the mixture was extracted with hexane (500 ml). The organic phase was separated, dried with sodium sulphate and concentrated *in vacuo* to ~200 ml. The precipitate was filtered off and washed with cold hexane (2 × 50 ml). Yield 77 g (47%).

Method B: A two-necked flask was charged with ionol (11 g, 50 mmol) and anhydrous diethyl ether (30 ml), and butyllithium (2 ml, 50 mmol) was added dropwise. After 30 min, $POCl_3$ (7 ml, 76 mmol) was added and the mixture was left overnight. Then, the mixture was filtered and concentrated and the product was used without further purification. The yield of 2,6-di-*tert*-butyl-4-methylphenyl phosphorodichloridate was quantitative (16.9 g). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.54$ (18H, s, *tert*-Bu), 2.36 (3H, d, $J = 2.38$, Me), 7.21 (2H, s, Ar). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 1.61$.

Pyridine (0.95 ml, 12 mmol) was added to a solution of 2,6-di-*tert*-butyl-4-methylphenyl phosphorodichloridate (3.37 g, 10 mmol) and ethanol (11 mmol) in methylene dichloride (6 ml). After 2 days, the mixture was concentrated, the residue was dissolved in pyridine (10 ml) and water (2 ml) was added. After 10 min, the pyridine was distilled off, the residue was dissolved in hexane (50 ml) and the solution was washed with 10% hydrochloric acid (50 ml). The organic phase was separated and the solvent was distilled off. The residue was recrystallised from hexane. The yield of 2,6-di-*tert*-butyl-4-methylphenyl ethyl phosphoric acid was 1.97 g (60%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.23$ (3H, t, $J = 7.02$, OCH_2CH_3), 1.42 (18H, s, *tert*-Bu), 2.27 (3H, s, Me (Ar)), 3.95 (2H, m, OCH_2CH_3), 7.05 (2H, s, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.80$ (d, $J = 7.31$, OCH_2CH_3), 31.86 (s, *tert*-Bu), 35.83 (s, Me (Ar)), 63.79 (d, $J = 5.12$, OCH_2CH_3), 127.56 (d, $J = 1.85$, 3-C), 132.87 (d, $J = 1.46$, 4-C), 142.25 (d, $J = 3.66$, 2-C), 146.00 (d, $J = 8.78$, 1-C). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = -5.17$. $C_{17}H_{29}O_4P$ calcd C 62.18, H 8.90; found C 62.07, H 8.81.

Synthesis of neodymium tris[(2,6-di-*tert*-butyl-4-methylphenyl ethyl) phosphate] (5)

A solution of KOH (6.74 g, 120 mmol) in water (100 ml) was added with stirring to a suspension of finely ground acid **4** (39.41 g, 120 mmol) in water (400 ml). After complete neutralisation, water (500 ml) was added and the resulting suspension was filtered and placed into a 2-litre flask equipped with a mechanical stirrer. Neodymium nitrate (16.65 g, 38 mmol) in water (200 ml) was added with stirring. After 4 h of stirring, the mixture was filtered and washed with water (4 × 200 ml). The precipitate collected on the filter was resuspended in benzene (500 ml) and filtered. The organic phase was dried over sodium sulphate. Benzene was evaporated *in vacuo* and the residue was recrystallised from 50 ml of hexane. The crystalline precipitate was filtered, washed with cold hexane (30 ml) and dried *in vacuo*. Yield 31.74 g (74%). $C_{51}H_{84}NdO_{12}P_3$ calcd C 54.38, H 7.52; found C 54.77, H 7.52.

Synthesis of lanthanum tris[bis(2,6-di-*tert*-butyl-4-methylphenyl ethyl) phosphate] (6)

A solution of KOH (1.77 g, 31.5 mmol) in water (10 ml) was added to a suspension of finely ground acid (10.34 g, 31.5 mmol) in water (100 ml) until the acid dissolved. $LaCl_3 \times 7H_2O$ (3.71 g, 10 mmol) in water (100 ml) was added to the obtained solution with stirring. After 4 h of stirring, the mixture was filtered and washed with water (3 × 100 ml). The precipitate was dried twice in a vacuum desiccator over $CaCl_2$ and then *in vacuo* to a constant weight. The resulting substance was dissolved in benzene (20 ml). The solution was concentrated to half its volume and added to pentane (10 ml). The precipitated crystals were filtered off, washed with pentane and dried *in vacuo*. Yield 5.1 g (51%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.48$ (12H, br.s, OCH_2CH_3), 1.16 (6H, br.s, OCH_2CH_3), 1.46 (36H, s, *tert*-Bu), 1.52 (18H, s, *tert*-Bu), 2.23 (12H, s, Me (Ar)), 2.32 (6H, s, Me (Ar)), 3.68 (8H, br.s, OCH_2CH_3), 3.99 (4H, br.s, OCH_2CH_3), 7.02 (8H, s, *m*-H (Ar)), 7.11 (4H, s, *m*-H (Ar)). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = -3.95$ (2P, L_2), −14.50 (4P, L_4). Anal. $C_{51}H_{84}LaO_{12}P_3$ calcd C 54.64, H 7.55; found C 54.49, H 7.89.

Synthesis of yttrium tris[bis(2,6-di-*tert*-butyl-4-methylphenyl ethyl) phosphate] (7)

A solution of KOH (0.35 g, 6.3 mmol) in water (5 ml) was added dropwise to a suspension of finely ground acid (2.07 g, 6.3 mmol) in water (20 ml) until the acid dissolved and the mixture was neutralised. $YCl_3 \times 6H_2O$ (0.61 g, 2 mmol) in water (10 ml) was added to the obtained solution with stirring. After 4 h of stirring, the mixture was filtered and washed with water (3 × 20 ml). The precipitate was dried twice in a vacuum desiccator over $CaCl_2$ and then *in vacuo* to a constant weight. The resulting substance was dissolved in hexane (20 ml). The solution was concentrated by 50% and cooled to −20 °C. The precipitated crystals were removed by filtration, washed with cooled pentane and dried *in vacuo*. Yield 1.21 g (60%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.45$ (6H, br.s, OCH_2CH_3), 0.88 (12H, br.s, OCH_2CH_3), 1.46 (36H, s, *tert*-Bu), 1.52 (18H, s, *tert*-Bu), 2.22 (12H, s, Me (Ar)), 2.30 (6H, s, Me (Ar)), 3.69 (8H, br.s, OCH_2CH_3), 3.93 (4H, br.s, OCH_2CH_3), 7.03 (8H, s, *m*-H (Ar)), 7.09 (4H, s, *m*-H (Ar)). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = -1.55$ (2P, L_2), −14.42 (4P, t, $J_{P-Y} = 9.91$, L_4). $C_{51}H_{84}O_{12}P_3Y$ calcd C 57.19, H 7.91; found C 57.05, H 8.30.

X-ray structure determination of 5–7

Single crystals of complexes 5–7 were obtained by the slow evaporation of saturated solutions in hexane. Experimental intensities were measured on a Bruker SMART APEX II diffractometer using graphite monochromatized Mo–Kα radiation ($\lambda = 0.71073$ Å) using a ω-scan mode. Absorption corrections based on measurements of equivalent reflections were applied.[23,24] The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (except for the *t*-Bu ligands in Y). As for Y, 36 methyl groups from the *t*-Bu ligands were refined isotropically due to the high thermal motion caused by free rotation along the CAr–CAlk bonds. In all the structures, hydrogen atoms were placed in calculated positions and refined using a riding model. The structure of Y contains two sites partially occupied by solvent *n*-hexane

Table 3 Crystal data, data collection and refinement parameters for **5**, **6** and **7**

Complex	5	6	7
Formula	$C_{102}H_{168}Nd_2O_{24}P_6$	$C_{102}H_{168}La_2O_{24}P_6$	$C_{108}H_{182}O_{24}P_6Y_2$
F_w	2252.66	2242.00	2228.18
Colour, habit	Colourless, block	Colourless, plate	Colourless, block
Cryst size, mm	0.20 × 0.15 × 0.10	0.10 × 0.05 × 0.01	0.25 × 0.20 × 0.20
Cryst syst	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T (K)	173	173	296
a (Å)	14.273(3)	14.344(3)	15.049(2)
b (Å)	14.921(3)	15.019(3)	20.351(3)
c (Å)	15.089(3)	15.110(3)	22.399(3)
α (°)	65.781(2)	65.955(3)	81.292(2)
β (°)	75.178(3)	74.968(3)	87.985(2)
γ (°)	82.048(3)	81.995(3)	76.987(2)
V (Å^3)	2831.1(9)	2868.9(9)	6606.5(16)
Z	1	1	2
ρ_{calc} (g cm^{-3})	1.321	1.298	1.120
μ (mm^{-1})	1.057	0.882	1.005
F(000)	1182	1176	2380
θ range (°)	1.48 to 28.00	2.34 to 25.50	2.28 to 25.50
Total no. of reflns	29 369	24 590	56 736
Unique reflns	13 617	10 682	24 561
R_{int}	0.0259	0.0587	0.0495
No. with $I > 2\sigma(I)$	11 903	7945	14 593
No. of variables	628	628	1052
R_1 ($I > 2\sigma(I)$)	0.0310	0.0444	0.0709
wR_2 (all data)	0.0827	0.0857	0.2282
GOOF on F^2	1.075	0.952	1.034
Largest diff peak/hole, e Å^{-3}	0.972/−0.456	0.968/−0.801	0.928/−0.603

molecules. The crystallographic data, data collection and refinement parameters for **5**, **6** and **7** are given in Table 3.

Preparation of the polymerisation catalyst from 5

A glass reactor was charged under argon with neodymium derivative **5** (0.113 g, 0.1 mmol) and hexane (7.5 ml). Butadiene (0.15 ml, 2 mmol) was recondensed (−78 °C). The mixture was cooled to −78 °C and a 1 M solution of DIBAL-H (1.5 ml) in hexane was added with stirring. After 1 h, a 0.83 M solution of $Me_3Al_2Cl_3$ (1 ml) in hexane was added to the reaction mixture. The mixture was stirred for 20 h at 20 °C and was then considered ready for use.

Butadiene polymerisation

The catalyst prepared from **5** (0.3 ml, 0.003 mmol) was placed into an ampoule in an argon flow. Hexane (17 ml) was added and butadiene (2.2 ml, 30 mmol) was recondensed (−78 °C). The ampoule was sealed and heated to 50 °C. After 2 h, the ampoule was opened and the reaction mixture was poured into methanol (50 ml). The precipitated polymer was collected, washed twice with methanol and dried *in vacuo*. Yield 1.61 g (99.4%).

Dilactide polymerisation

A glass ampoule was charged with a stirrer bar, D,L-dilactide (1.000 g, 6.9×10^{-3} mol) and the corresponding metal triphosphate (6.9×10^{-5} mol) was evacuated *in vacuo* (2×10^{-1} mmHg), filled with dry argon, and covered with a septum. Toluene (4 ml) was then added. In another dry ampoule covered with a septum, a solution was prepared by mixing a 1.9 M solution of Et_3Al (1.4 ml) in toluene with toluene (8.6 ml) and isopropanol (0.10 ml). After stirring for 3 min, 0.5 ml of this solution was withdrawn into the dilactide ampoule. The ampoule was sealed and placed into a bath preheated to the desired temperature and kept for 6 h. Then, the ampoule was opened and the solvent was evaporated. The small amount of the resulting substance was dissolved in $CDCl_3$. Conversion of the dilactive was determined by comparison of the integration of the signals of the polymer with the corresponding signals of the residual dilactide.

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