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# Synthesis, Characterization, and Activity of Yttrium(III) Nitrate Complexes Bearing Tripodal Phosphine Oxide and Mixed Phosphine–Phosphine Oxide Ligands

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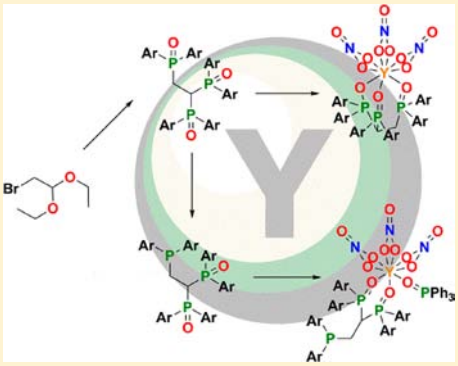
Supporting Information

**ABSTRACT:** A series of four tripodal phosphine oxide ligands, $(OPR_2)_2CHCH_2POR_2$ (**1a–1d**), and four mixed phosphine–phosphine oxide ligands, $(OPR_2)_2CHCH_2PR_2$ (**3a–3d**), were synthesized and coordinated to yttrium to produce $Y(NO_3)_3[(OPR_2)_2CHCH_2POR_2]$ (**2a–2d**) and $Y(NO_3)_3[(OPR_2)_2CHCH_2PR_2](OPPh_3)$ (**4a–4d**) complexes. The previously reported ligand **1a** and unknown phosphine oxide ligands **1b–1d** were generated in an unprecedented trisubstitution reaction of bromoacetaldehyde diethyl acetal, while the novel partially reduced ligands **3a–3d** were synthesized from **1a–1d** according to a known literature protocol for the selective monoreduction of bisphosphine oxides. The neutral yttrium complexes **2a–2d** are nine-coordinate and display a tricapped trigonal-prismatic geometry. Complexes **4a–4d** are also neutral, nine-coordinate species and have a pendant phosphine functionality, which provides the potential to form bimetallic early–late transition-metal complexes. Additionally, yttrium complexes **2a–2d** were activated with base and tested for the ring-opening polymerization of $\varepsilon$-caprolactone, but the results showed that base by itself was significantly more effective than the yttrium species investigated.




## INTRODUCTION

Yttrium is an industrially relevant element with applications as a lasing medium for lanthanide-doped yttrium–aluminum garnet (YAG) solid-state lasers[1−4] and as an additive to refractory materials for the formation of adherent metal oxide layers.[5] In addition, the radioisotope $^{90}Y$ has been found to be useful in radiotherapeutical treatments for various types of cancer.[6−11] Despite its industrial significance, yttrium is one of the least studied transition metals. Only a handful of studies have explored the ability of this metal to catalyze chemical transformations, which include $\alpha$-olefin polymerization,[12−18] asymmetric hydroamination of alkenes,[19,20] hydrosilylation of alkenes,[21,22] and several other reactions.[23−25] More recently, however, interest in yttrium has increased because of its activity in the ring-opening polymerization (ROP) of cyclic esters to form biodegradable polyester polymers,[26−38] which have promising medical applications.[39−42]

A noteworthy feature of yttrium is its similarity to lanthanide rare-earth metals.[43−46] The most common oxidation state of yttrium is 3+, and its ionic radius is comparable to those of analogous trivalent lanthanides (intermediate between $Dy^{3+}$ and $Ho^{3+}$).[43−46] Because of these parallels, yttrium exhibits chemical and physical properties similar to those of lanthanide metals, with the exception that, unlike most trivalent lanthanides, yttrium is diamagnetic and monoisotopic ($^{89}Y$ = 100% abundant) and has a spin of $I = {}^1/_2$. This makes yttrium an ideal model for investigating the behavior of lanthanide metals.

When spent nuclear fuels are reprocessed, the irradiated materials are dissolved in nitric acid.[47,48] Then, using liquid–liquid extraction methods, a crucial part of the procedure is the removal of lanthanide metals from actinides.[49−51] Strong oxygen donors bind the oxophilic lanthanides, and it has been shown that polyfunctional extractants are more efficient than their monofunctional analogues.[47,48,52] A commonly used ligand in the TRUEX (TRansUraniumEXtraction) process is carbamoylphosphine oxide, which binds metal cations through amide and phosphine oxide functionalities.[53,54] Previous studies have shown, however, that phosphine oxides are better donors for lanthanides than amides,[55−59] and it would be beneficial to develop polyphosphine oxide ligands for liquid–liquid extraction applications. Because of its similarity to lanthanide rare-earth metals, yttrium is a perfect candidate for testing the effectiveness of new extraction ligands, and because of its NMR handles, any metal complexes thus formed would be much easier to follow and characterize.

We have previously reported the syntheses of diarylphosphorylacetaldehyde diethyl acetals as convenient precursors for the production of phosphonium dimers.[60] The yield of this process was somewhat low, indicating that a substantial amount of the starting materials was either decomposing or undergoing unwanted side reactions. Upon crystallization of the major side product of this reaction, it was found that 1,1,2-tris(diarylphosphoryl)ethane was being produced (see Scheme

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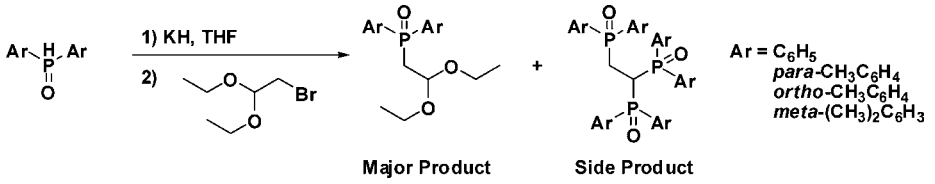
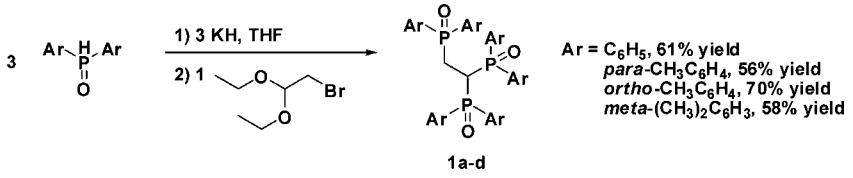
**Scheme 1. Synthesis of Diarylphosphorylacetaldehyde Diethyl Acetal and 1,1,2-Tris(diarylphosphoryl)ethane**




**Scheme 2. Synthesis of Ligands 1a−1d Starting from Diarylphosphine Oxides**



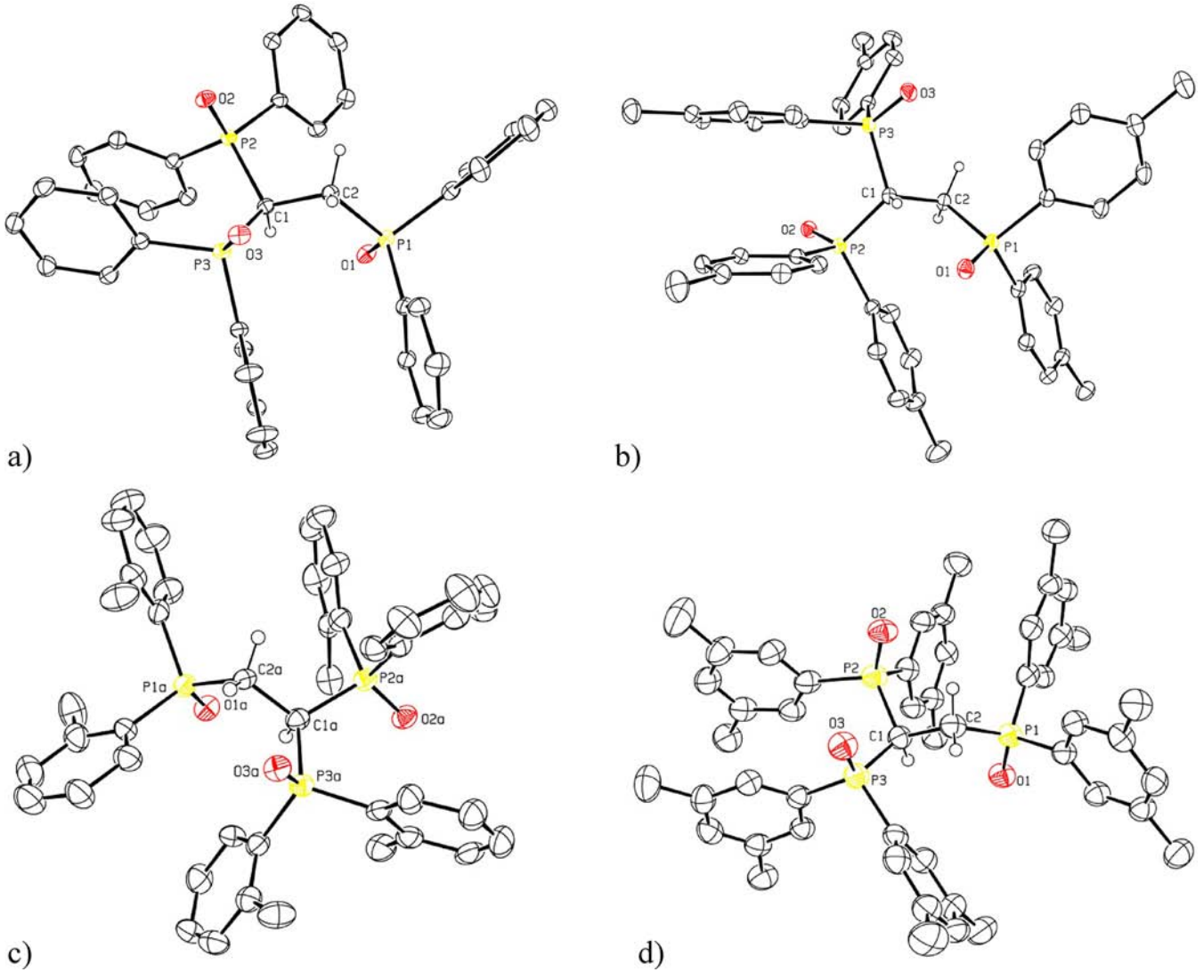




**Figure 1.** ORTEP3 representation (thermal ellipsoids at 50% probability; most of the hydrogen atoms are omitted for clarity) and atom numbering for (a) **1a**, (b) **1b** (the solvent is also omitted for clarity), (c) **1c** (the solvent is also omitted for clarity), and (d) **1d**.

1). This polyfunctional phosphine oxide ligand was immediately identified as a potential extraction agent for nuclear fuel treatment. In this paper, we describe the synthesis of 1,1,2-tris(diarylphosphoryl)ethane ligands and their reactions with yttrium. In addition, we endeavored to reduce the phosphine oxide ligands and coordinate the resulting mixed phosphine−phosphine oxide ligands to yttrium. Furthermore, several yttrium complexes were activated with base, and their activity toward the ROP of $\varepsilon$-caprolactone was investigated. With respect to nomenclature, throughout this paper, compounds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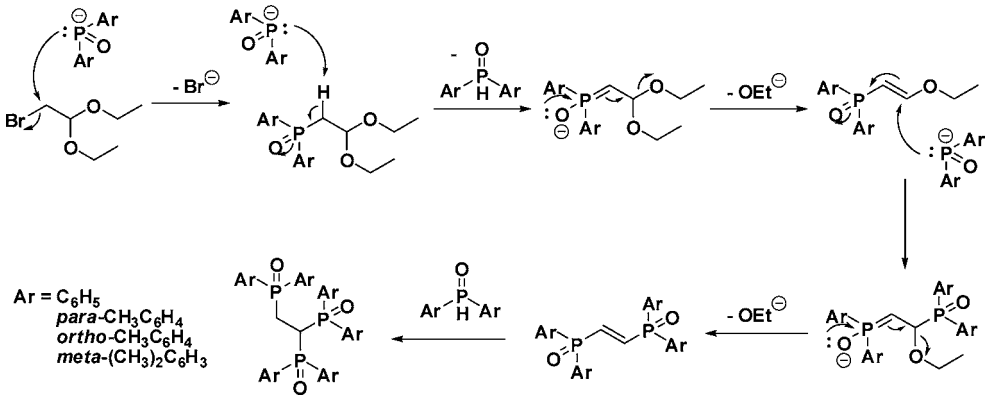
**Scheme 3. Proposed Mechanism for the Formation of Ligands 1a−1d**




will be named according to their aryl substitution pattern: **a** for phenyl; **b** for *p*-tolyl; **c** for *o*-tolyl, and **d** for *m*-xylyl.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Tridentate Phosphine Oxide Ligands 1a−1d.** Compounds **1a−1d** were prepared using an unprecedented trisubstitution reaction where 3 equiv of diarylphosphine oxide were deprotonated with KH and combined directly with bromoacetaldehyde diethyl acetal to yield white, air-stable powders in moderate yields (55−70%). In this reaction, the bromide and ethoxide groups of bromoacetaldehyde diethyl acetal have been replaced by diarylphosphoryl functionalities (see Scheme 2). Compound **1a** has been reported previously and was prepared via several alternative synthetic routes employing vinyl chlorides[61,62] but was never fully characterized. Moreover, various trisubstitution reactions of bromoacetaldehyde diethyl acetal have previously been reported, but these were two-step processes that required the use of an acid to in situ deprotect the protected aldehyde to facilitate the loss of ethanol and the incorporation of the desired functional groups.[63−67]

The $^{31}P\{^{1}H\}$ NMR spectra of compounds **1a**, **1b**, and **1d** all show characteristic peaks in the phosphine oxide region. The two equivalent phosphorus nuclei display a doublet around 32 ppm and are coupled to the remaining inequivalent phosphorus nucleus, which displays a triplet around 29 ppm. The $^{31}P\{^{1}H\}$ NMR spectrum of **1c**, on the other hand, displays a triplet around 32 ppm, much like the other compounds, but the doublet for the two equivalent phosphorus nuclei is missing. In its place is a broad singlet at 40 ppm, which arises from the coalescence of resonances for interconverting rotamers in solution; the rate of exchange is a rapid process on the NMR time scale. This type of behavior has been seen previously with bulky *o*-tolyl substituents,[60] which are known to have restricted rotation about the C−P bond (barriers of rotation of up to 19.5 kJ/mol).[68] The $^{1}H$ NMR spectra of compounds **1a−1d** also exhibit several diagnostic peaks. The proton $\alpha$ to the two equivalent phosphorus centers displays a unique multiplet in the range between 5.2 and 4.4 ppm, as do the protons $\alpha$ to the lone phosphorus center, between 3.5 and 2.9 ppm.

In addition to NMR experiments, compounds **1a−1d** were characterized in the solid state utilizing single-crystal X-ray diffraction studies (see Figure 1). All of the 1,1,2-tris(diarylphosphoryl)ethane ligands display typical bond lengths and angles, with the exception of the P2−C1−P3 and P1−C2−C1 bond angles. Presumably, the steric bulk of the two equivalent diarylphosphoryl moieties distorts the geometry of the adjacent carbon atom, opening the P2−C1−P3 bond angle wider than the optimal tetrahedral angle of 109.45°. Similarly, the steric bulk of the phosphoryl groups also opens the P1−C2−C1 bond angle. The general trend for the sizes of the P2−C1−P3 and P1−C2−C1 bond angles supports this theory, with the most sterically encumbered phosphorus group, *o*-tolyl in compound **1c**, producing the largest angles, 118.8(9)° and 113(1)°, respectively (for further notable bond lengths and angles, see the Supporting Information, Table S1). Another interesting feature evident in the crystal structures is $\pi-\pi$ stacking between the aryl groups of the different phosphorus functionalities. The aryl rings of both the equivalent and inequivalent phosphoryl groups can be seen aligning themselves parallel to each other, and in the case of **1c**, the bulky substituents are oriented away from each other to minimize unfavorable steric interactions.

The mechanism of formation for compounds **1a−1d** is, at the same time, intriguing and poorly understood. Several attempts were made to generate structures similar to the polyfunctional phosphine oxides by first installing a unique functional group (phosphino or amino) in place of the bromide on the bromoacetaldehyde diethyl acetal precursor. Then, the isolated, monosubstituted product was subjected to an excess of deprotonated diarylphosphine oxide in an endeavor to replace the ethoxides with phosphoryl moieties. Unfortunately, every effort resulted in no incorporation of the phosphine oxide functionalities and in the recovery of the monosubstituted starting material. If, on the other hand, diarylphosphorylacetaldehyde diethyl acetal was exposed to 2 equiv of deprotonated diarylphosphine oxide, full conversion to the trisubstituted product was achieved.

It is therefore believed that the initial substitution of bromine by phosphine oxide is crucial in initiating the trisubstitution process (Scheme 3). Once incorporated into the carbon backbone, a phosphoryl group would greatly increase the acidity of the $\alpha$-carbon through inductive effects, as well as through resonance stabilization of the conjugate base. This, in conjunction with the fact that the medium is extremely basic, makes it feasible for a deprotonated diarylphosphine oxide to abstract a proton from the $\alpha$-carbon, with the resulting carbanion being stabilized by the adjoining phosphoryl group. Subsequently, in an E1cb fashion, an ethoxide could be eliminated with concomitant C−C double-bond formation. The unsaturated intermediate generated, however, would be susceptible to nucleophilic attack by a phosphoryl anion at the more electrophilic carbon, which would regenerate a resonance-stabilized carbanion at the previously deprotonated carbon.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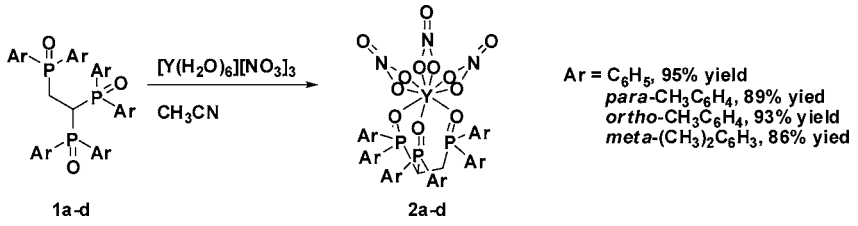
**Scheme 4. Synthesis of Yttrium Complexes 2a−2d Using Ligands 1a−1d**



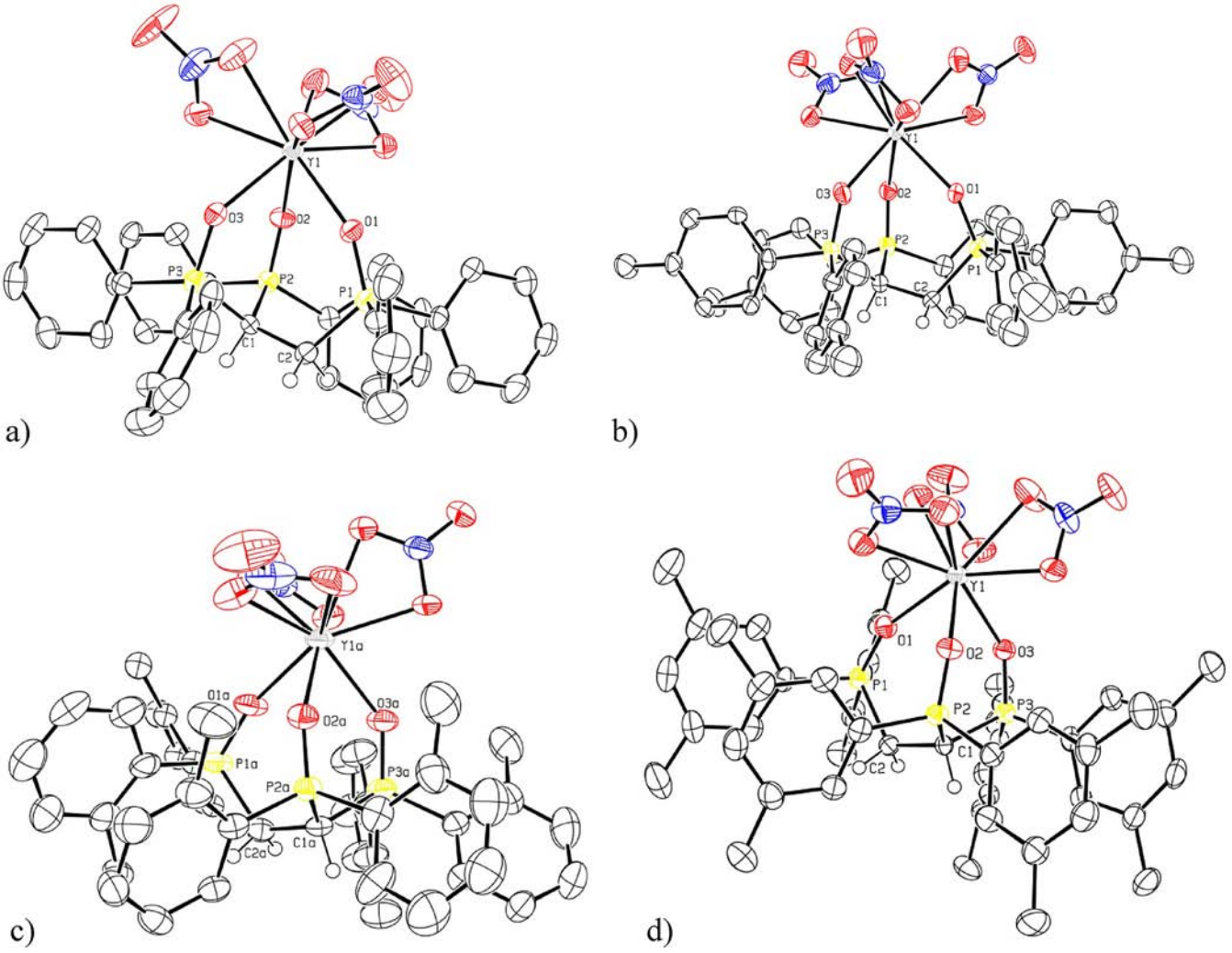




**Figure 2.** ORTEP3 representation (thermal ellipsoids at 50% probability; the solvent and most of the hydrogen atoms are omitted for clarity) and atom numbering for **2a−2d**.

Following this, another E1cb-type reaction could eliminate the last ethoxide group and produce a 1,2-bis(diarylphosphoryl)-ethylene species. In the last step, protonated diarylphosphine oxides in solution could react with the disubstituted intermediate and hydrophosphinate the double bond, thus generating the observed polyfunctional phosphine oxide products.

Efforts have been made to isolate some of the possible intermediates in the proposed mechanism, with emphasis put on trapping of the 1,2-bis(diarylphosphoryl)ethylene species, but these attempts have met with little success to date. Despite control of the stoichiometry of the reactants and the addition of only 1 equiv of deprotonated phosphine oxide at a time at −78 °C and then warming to room temperature, the only products isolated were the trisubstituted ligand and the starting materials. If trimethylsilane was added in order to trap either of the proposed unsaturated intermediates, the only products observed were the 1,1,2-tris(diarylphosphoryl)ethane species, the reactants, and some unrecognizable decomposition products. Indirect evidence, however, for a 1,2-bis-(diarylphosphoryl)ethylene intermediate was obtained by combining di-*o*-tolylphosphorylacetaldehyde diethyl acetal with 2 equiv of deprotonated diphenylphosphine oxide. Two products were evident in the NMR spectrum of the crude product: one with a triplet and a doublet corresponding to a product with geminal diphenylphosphoryl moieties and one with two sets of doublet of doublets and one doublet corresponding to a product with germinal diphenylphosphoryl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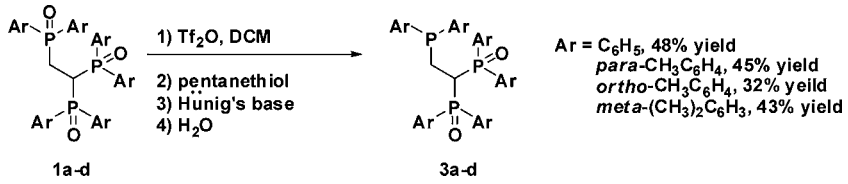
Scheme 5. Synthesis of Ligands 3a−3d Using Ligands 1a−1d




and di-*o*-tolylphosphoryl functionalities. Sequential displacement of ethoxy groups would only generate the former product, while hydrophosphination of an unsaturated intermediate could produce both of the products that were seen. Further studies probing the exact mechanism of the formation for compounds **1a−1d** are needed.

**Synthesis and Characterization of Yttrium Complexes 2a−2d.** Popovici et al. have recently reported the synthesis of bis(phosphinic amide)phosphine oxide ligands, which they coordinated to yttrium, a well-established model for the rare-earth metals, in order to explore whether or not their ligands were suitable for nuclear fuel extraction applications.[69] These ligands had three P−O double-bond moieties, much like our tripodal phosphine oxide compounds **1a−1d**, and as such, we thought that our ligands would exhibit similar coordination modes. To generate yttrium complexes, 1 equiv of compound **1a**, **1b**, **1c**, or **1d** was dissolved in acetonitrile and a solution of $Y(H_2O)_6(NO_3)_3$ in acetonitrile was added (see Scheme 4). The mixtures were stirred for 15 min to yield the corresponding complexes **2a−2d**, which precipitated out of solution as white, air-stable powders in very good yield (85−95%). These white powders were insoluble in most solvents, except for methanol and dimethyl sulfoxide (DMSO), despite being neutral species. If an excess of the tridentate ligand was used, however, the complexes remained soluble in acetonitrile and could be precipitated out of solution with less polar solvents such as ether.

Because of the insolubility of complexes **2a−2d** in solvents other than methanol or DMSO, which showed only free displaced ligands in the NMR spectra, the yttrium species could not be characterized by conventional spectroscopic methods. Fortunately, crystals of the yttrium complexes were easily grown from the slow diffusion of ether into an acetonitrile solution containing 2 equiv of ligand **1a**, **1b**, **1c**, or **1d** and 1 equiv of yttrium nitrate hexahydrate. Accordingly, **2a−2d** were all characterized by single-crystal X-ray diffraction studies.

The yttrium compounds were found to be nine-coordinate neutral species that displayed a distorted tricapped trigonal-prismatic geometry. The polyfunctional phosphoryl ligands form three vertices of the trigonal prism, while the three bidentate nitrate ligands occupy the other three vertices of the prism, as well as the three capping positions outside of the rectangular faces of the trigonal prism (see Figure 2). Moreover, in the crystal structures for **2a−2d**, the P2−C1−P3 bond angle is constrained to be around 110° because of coordination of the oxygen moieties to the yttrium metal center; for all of the ligands, this represents a compression of this angle from the free ligand form. In addition, the P1−C2−C1 angle has been drastically increased upon coordination to the metal. It increased from 107−113° in **1a−1d** up to 116−119° in **2a−2d** in order to accommodate the tricapped trigonal-prismatic geometry enforced by the yttrium center (for further notable bond lengths and angles, see the Supporting Information, Table S2). Furthermore, $\pi-\pi$ stacking between the aryl groups of the different phosphorus functionalities is evident in the solid-state structures. The aryl rings are aligned parallel to each other, and for **2c**, the methyl substituents are oriented away from each other to minimize unfavorable steric interactions.

An exciting feature of these systems is that the solubility of the complexes in organic solvents can be switched on and off depending on the concentration of the ligand present. When an excess of the ligand is present in solution, the yttrium nitrate species are freely soluble in acetonitrile and other polar organic solvents. If, on the other hand, there is a 1:1 ratio of yttrium to ligand, then the metal complexes rapidly precipitate out of solution. By control of the stoichiometry of the ligand versus the metal center in solution, a desired metal cation could be taken up into an organic solvent and then crashed out later with the addition of more of the metal precursor to isolate very pure complexes. These features of this polyfunctional phosphine oxide system would greatly expedite the removal and subsequent purification of lanthanides in nuclear fuel reprocessing.

Variable-temperature NMR studies probing the nature of the 2:1 mixtures were carried out, but the results provided little insight as to what is occurring in solution. The $^{31}P$ NMR spectra showed at least 12 separate broad peaks at −40 °C in deuterated acetonitrile, indicating that the system is dynamic and involves at least four interconverting species.

**Synthesis and Characterization of Tridentate Mixed Phosphine−Phosphine Oxide Ligands 3a−3d.** After the synthetic route for generating the 1,1,2-tris(diarylphosphoryl)-ethane ligands was shown to be a general method for producing polyphosphine oxide compounds and it had been established that the sterically bulky ligands could be accommodated on transition metals, it was thought that the fully reduced forms of the ligands, which would resemble a fusion of bis-(diarylphosphino)methane and 1,2-bis(diarylphosphino)-ethane, would be interesting synthetic targets. All conventional methods of reducing phosphine oxides were employed, but all attempts to reduce compounds **1a−1d** resulted in fragmentation of the ligands. Regardless of the reducing agents or the conditions utilized, the production of diarylphosphines, diarylphosphine oxides, and other decomposition products was always seen. It is known in the literature that the bridging carbon of bis(diphenylphosphino)methane is prone to deprotonation,[70−74] and analogously it was believed that the increased acidity of the carbon with two phosphoryl moieties was a major contributor to the instability of compounds **1a−1d** under reduction conditions. It was anticipated that once one or more of the phosphine oxides were reduced, the $pK_a$ of the acidic C−H bond would increase greatly, which would impart more stability to the ligands and allow for the subsequent reduction of the remaining phosphine oxide functionalities utilizing conventional methods. Extremely mild, weakly basic conditions for the partial reduction of phosphine oxides were therefore investigated.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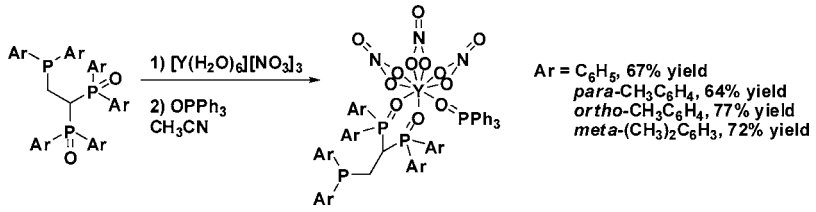
**Scheme 6. Synthesis of Yttrium Complexes 4a−4d Using Ligands 3a−3d**




In 2008, Jenkins et al. reported a procedure for the selective monoreduction of bisphosphine oxides employing *N*,*N*-diisopropylethylamine, an extremely bulky base, and 1-pentanethiol as the reductant.[75] The reaction conditions are extremely mild, and various test reactions showed that the crowded amine base was unable to deprotonate the sterically encumbered acidic carbon atom of compounds **1a−1d**, even at elevated temperatures. Using the same synthetic procedure outlined in the paper, previously unknown partially reduced compounds **3a−3d** were generated in modest yields (32−48%) and isolated as white powders (see Scheme 5).

The $^{31}P\{^{1}H\}$ NMR spectra of compounds **3a−3d** were remarkably similar to those of compounds **1a−1d** with one significant difference: the phosphoryl triplet around 29−32 ppm representing the single, nonequivalent phosphine oxide group was shifted to the negative region (between −12 and −37 ppm), indicating that the phosphine oxide functionality was reduced to a phosphine moiety. The doublets around 32−40 ppm, however, remained, for the most part, unchanged, 30−38 ppm, and, additionally, **3c** displayed a doublet in this region instead of a broad singlet, as was seen for **1c**, signifying that rotation about the P−C bonds had a lower barrier for the partially reduced ligand. It is interesting to note that the phosphine oxide reduction was completely chemoselective, as seen by $^{31}P$ NMR; only the nonequivalent phosphoryl group was reduced. Although the yields of these reactions are quite low, which can be attributed to an incomplete reaction as large amounts of starting material are recovered, there is no evidence of any significant reduction of the other phosphoryl moieties in the reaction mixture or the crude products. This behavior may be due to the steric encumbrance of the other phosphoryl functionalities, which precludes their reduction.

Jenkins et al. invoked a mechanism in which a thiolate attacks a phosphorus atom, generating a phosphonium intermediate.[75] Another equivalent of thiolate then either directly attacks the phosphorus again and the two thiolates reductively eliminate or the second thiolate attacks the coordinated thiolate directly, thus reducing the phosphorus center.[75] In both cases, the least crowded phosphorus moiety would be most available for attack by the thiolate reductants, which explains the selectivity of the reaction for the reduction of the most accessible phosphoryl group.

The $^{1}H$ NMR spectra of compounds **3a−3d** were also nearly identical with those of **1a−1d**. The mixed phosphine−phosphine oxide ligands had very similar distinctive peaks for the protons $\alpha$ to the phosphorus atoms, which were shifted only moderately from their fully oxidized forms. The proton $\alpha$ to the two equivalent phosphoryl functionalities displayed a unique multiplet between 4.1 and 3.1 ppm, while the protons $\alpha$ to the reduced phosphorus center appeared as triplets of doublets, around 3.0 to 2.4 ppm.

With the partially reduced ligands in hand, further attempts to fully reduce the ligands met with little success. As in the case of the completely oxidized forms **1a−1d**, all conventional methods for reducing phosphine oxides were employed, but all reducing conditions led to the decomposition of compounds **3a−3d**, as seen previously. Although a disappointing result, the partially reduced ligands are interesting in and of themselves. The mixed phosphine−phosphine oxide compounds contain two very different types of donor groups; the phosphine oxides are very hard donors, while the phosphine functionalities are much softer. These ligands therefore have the potential to support early−late bimetallic transition-metal systems, where the oxygen moieties coordinate early transition metals and the phosphines preferentially bind late transition metals. Furthermore, because the phosphine oxide functionalities are such poor donors for late transition metals, compounds **3a−3d** could find applications in catalytic systems where multidentate hemilabile ligands are desirable. Several rhodium- and palladium-based catalysts employing mixed phosphine−phosphine oxide ligands have been reported that were successful in the catalytic hydrogenation alkenes and in Suzuki coupling, respectively.[76] In both cases, the phosphine moiety provided a firm anchor to the metal center and the phosphine oxide displayed a dynamic behavior, which helped the catalysts switch between different states.[76]

**Synthesis and Characterization of Yttrium Complexes 4a−4d.** In order to demonstrate the selectivity of the different phosphorus functionalities of ligands **3a−3d** for the binding of transition metals, yttrium complexes of the mixed phosphine−phosphine oxide ligands were synthesized. A total of 1 equiv of **3a**, **3b**, **3c**, or **3d** was dissolved in acetonitrile, and a solution of $Y(H_2O)_6(NO_3)_3$ in acetonitrile was added. $^{31}P$ NMR spectra of the reaction mixtures revealed that two products were generated in solution, which had very similar doublets of doublets representing coordinated phosphoryl groups, between 40 and 30 ppm ($^{2}J_{YP}$ approximately 6 Hz) and nearly identical triplets corresponding to uncoordinated diarylphosphine in the negative region. It was thought that the two species in solution arose from acetonitrile or water from the starting material coordinating to a vacant site on the metal center. The addition of molecular sieves to the reaction mixtures did cause one of the species in solution to become more prevalent, while the other diminished in intensity, but the conversion process was slow, taking several days without reaching completion. A total of 1 equiv of triphenylphosphine oxide in acetonitrile was therefore added to the reaction mixtures to readily substitute for acetonitrile or water on yttrium (see Scheme 6). Complexes **4a−4d**, with three phosphine oxide ligands and a dangling diarylphosphine moiety, were isolated as white powders in moderate yields (63−77%).

The $^{31}P$ NMR spectra of yttrium complexes **4a−4d** displayed a major product in solution as well as several minor products all with similar chemical shifts. The phosphorus peaks were somewhat broad, indicating that an equilibrium between the different species in solution was occurring on a time scale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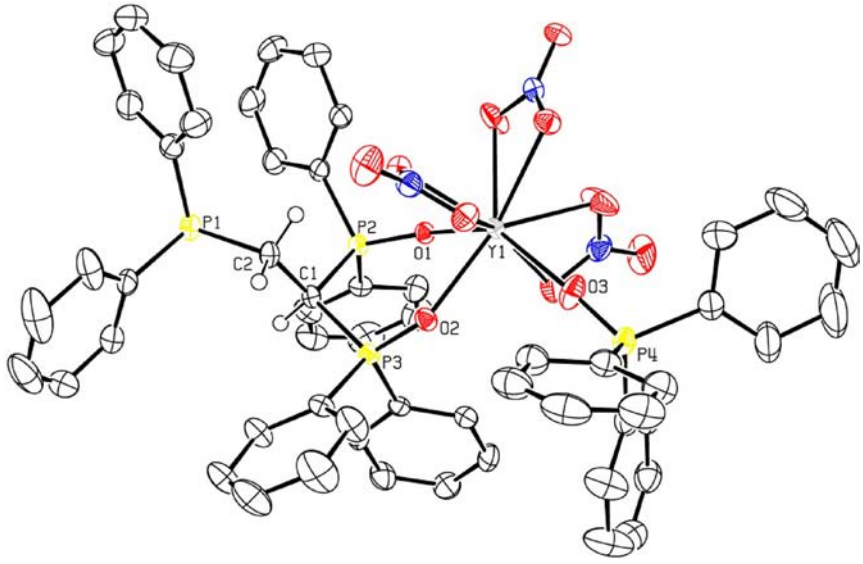


**Figure 3.** ORTEP3 representation (thermal ellipsoids at 50% probability) and atom numbering for **4a**. Most of the hydrogen atoms are omitted for clarity.

comparable to that of the NMR experiment. For **4c** especially, the phosphorus peaks were quite broad because not only was an equilibrium near the time scale of the NMR experiment occurring between the different structural isomers but also an interconversion of various rotamers. Variable-temperature NMR studies on **4a**−**4d** illustrated that these processes could be frozen out, with all of the minor species, as well as the peaks representing the phosphoryl rotamers for **4c**, becoming more distinct. Three separate sets of peaks could be identified for **4a**−**4d**: the pendant diarylphosphine functionality (−44 to −10 ppm), the equivalent phosphoryl groups (around 40 ppm), and the triphenylphosphine oxide ligand (around 36 ppm). The phosphoryl functionalities for **4a**−**4c** coupled to the yttrium center ($^2J_{YP}$ approximately 6 Hz) as well as the pendant diarylphosphine throughspace and thus exhibited a doublet of doublets, whereas **4c** did not show any coupling even at −60 °C. In addition, the triphenylphosphine oxide ligand coupled to the yttrium center and displayed a doublet for all of the yttrium complexes ($^2J_{YP}$ approximately 10 Hz).

For **4a**−**4d**, only one broad peak was seen in the negative region, which we believe represents overlapping signals for the reduced phosphorus centers of the major and minor species in solution. It is also believed that the different species in solution are very fluxional and the different phosphorus peaks represent interconverting structural isomers that differ in the arrangement of the nitrate and triphenylphosphine oxide ligands, as well as yttrium species that differ in the number of triphenylphosphine oxide ligands on the metal.

Additional variable-temperature NMR studies were conducted to further elucidate what was occurring in solution. We found that the addition of 1 or 2 equiv of $OPPh_3$ increased the intensity of several signals assigned to minor species in solution, but not all of them. This indicated that some of the species in solution do arise from different numbers of $OPPh_3$ binding to the same metal center, a redistribution process well-known in the literature,[77,78] but some of the minor species arise from different arrangements of the nitrate and phosphine oxide ligands.

The $^1$H NMR spectra of **4a**−**4d** supported these findings in that the peaks were fairly broad and the different species in solution could not be differentiated from one another because their chemical shifts were nearly identical and overlapped. The distinctive peak for the protons $\alpha$ to the diarylphosphine was found to be between 4.5 and 3.8 ppm, while the distinctive peak for the proton $\alpha$ to the phosphoryl groups was found to be between 3.2 and 2.4 ppm, much like compounds **1a**−**d** and **3a**−**3d**. Moreover, for **4a**−**4c**, the proton $\alpha$ to the diarylphosphine moiety coupled to the phosphorus and adjacent proton and therefore exhibited a doublet of triplets, while **4c** displayed only a broad signal at −40 °C.

Crystals of **4a** suitable for single-crystal X-ray diffraction studies were grown from a concentrated solution of the complex in acetonitrile. It is evident from the crystal structure that the reduced phosphorus functionality is indeed pendant and the phosphine oxide functionalities preferentially bind the early transition metal (see Figure 3). Much like **2a**−**2d**, the yttrium complex is nine-coordinate and has a distorted tricapped trigonal-prismatic geometry. Three of the vertices of the trigonal prism are occupied by nitrate oxygen atoms, while the other three vertices are comprised of the triphenylphosphine oxide ligand, a nitrate oxygen atom, and one phosphoryl moiety of the mixed phosphine−phosphine oxide ligand (O3═P4). The three capping positions outside of the rectangular faces of the trigonal prism are occupied by two nitrate oxygen atoms and the remaining phosphoryl group of ligand **3a**. Furthermore, the P2−C1−P3 bond angle is more compressed for **4a** than for **2a**, 108.4(1)° versus 110.6(5)°, and the P1−C2−C1 angle, which is no longer constrained by three sites binding to the metal center, has relaxed from 119.6(9)° to 111.8(5)° (for further notable bond lengths and angles, see the Supporting Information, Table S3). When crystals of **4a** were dissolved in an NMR solvent and a $^{31}$P NMR spectrum was taken, the same fluxional behavior that was discussed previously was seen. This supports the hypothesis that the minor species present in solution are the result of rapid equilibria between various closely related structural isomers and that this fluxional behavior is a product of dissolving the complexes in a solvent.

With respect to the possibility of using ligands **3a**−**3d** for the synthesis of early−late bimetallic complexes, it has been shown in this work that the hard phosphoryl functionalities of the


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partially reduced ligands preferentially bind early transition metals and that the softer phosphine moieties do not. It is known in the literature that heterobimetallic systems can have unique reactivity that involves the cooperation of both metals, where electron-poor early transition metals and electron-rich late transition metals create an ideal environment for the heterolytic cleavage of polar bonds.[79−84] With these ligands in hand, we are currently investigating their properties for the synthesis of heterobimetallic systems and the application of these systems for the cooperative, heterolytic cleavage of polar substrates.

**ROP of ε-Caprolactone Utilizing 2a−2d.** Several yttrium complexes have been reported in the literature that are effective catalysts for the ROP of ε-caprolactone.[85−94] All of the yttrium catalysts described employ various bases coordinated to the metal center that are used to initiate the polymerization reaction. It is also known that anionic initiators themselves can catalyze the ROP of ε-caprolactone and that the nature of the products depends on the concentration of the monomer in solution: at low concentrations, cyclic oligomers form, but at higher concentrations, linear polymers are preferred.[95−97]

In order to generate catalysts capable of ROP, complexes **2a−2d** were preactivated with base before being exposed to a solution of ε-caprolactone. These systems were extremely slow, often taking over 1 day to reach complete conversion, and we saw a general trend that, as the electron-donating ability of the ligands increased, there was a concomitant increase in the activity of the catalysts (see the Supporting Information, Table S6). In addition, the polydispersity indexes (PDIs) generated by the yttrium systems were quite large, which indicates that the catalysts most likely do not perform living polymerization. Our findings also suggest, however, that base alone is sufficient to effectively catalyze the ROP of ε-caprolactone under the reaction conditions; KO$^t$Bu was actually more effective than all of our activated complexes by a significant amount. This indicates that **2a−2d** may not be catalysts at all but may act as base inhibitors, and the elevated activity of the more electron-rich systems could reflect a lower affinity for binding alkoxide base.

## CONCLUSION

We have synthesized a series of four phosphine oxide ligands, **1a−1d**, and four mixed phosphine−phosphine oxide ligands, **3a−3d**, which were coordinated to yttrium to generate early-transition-metal complexes **2a−2d** and **4a−4d**. The tripodal phosphine oxide ligands **1a−1d** were produced in an unexpected trisubstitution reaction of bromoacetaldehyde diethyl acetal and were identified as promising extraction agents for nuclear fuel treatment. Although the mechanism of this process is currently unknown, it is suspected that the products are generated through a series of E1cb reactions and unsaturated intermediates, all of which depend on the crucial first substitution of a bromide with a phosphoryl functionality. In order to investigate the ability of the trisphosphine oxide ligands to act as lanthanide extraction agents, their coordination behavior toward yttrium, a well-established model for the rare-earth metals, was examined. The yttrium complexes thus synthesized, **2a−2d**, were neutral nine-coordinate species that displayed a tricapped trigonal-prismatic geometry, and their solubility in organic solvents could be tuned depending on the amount of ligand in solution. Attempts were made to reduce compounds **1a−1d**, but all conventional methods for reducing phosphine oxides met with little success. Only the extremely mild reduction conditions reported by Jenkins et al. employing 1-pentanethiol and triflic anhydride for the partial reduction of diphosphine oxides were successful in partially reducing the ligand without causing ligand fragmentation.[75] The conditions utilized were chemoselective for the reduction of the unique, less-crowded phosphoryl functionality, and the resulting mixed phosphine−phosphine oxide ligands, **3a−3d**, were recognized as ligands capable of supporting early−late bimetallic complexes. To test the selectivity of the different phosphorus moieties of the partially reduced ligands for the binding of transition metals, compounds **3a−3d** were also bound to yttrium. The yttrium complexes generated, **4a−4d**, were found to be neutral, nine-coordinate species, much like **2a−2d**, but with a pendant phosphine functionality. This finding supports the hypothesis that the hard phosphoryl functionalities of **3a−3d** preferentially bind early transition metals, while the softer phosphine moieties do not, and gives promise for utilizing these ligands to synthesize heterobimetallic systems. Yttrium complexes **2a−2d** were activated with base, and their activity for the ROP of ε-caprolactone was investigated. It was found that the catalytic systems were extremely slow and that the base by itself was actually a superior catalyst to the activated yttrium complexes, which could, in fact, be acting as base inhibitors.

## EXPERIMENTAL SECTION

**General Considerations.** All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk-line and glovebox techniques unless stated otherwise. All solvents were degassed and dried using standard procedures prior to all manipulations and reactions unless stated otherwise. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Sigma Aldrich, degassed, and dried over activated molecular sieves prior to use. ε-Caprolactone used for polymerization experiments was degassed and dried over activated molecular sieves prior to use. All other reagents were purchased from commercial sources and utilized without further purification. KO$^t$Bu used for the polymerization experiments was purchased from Sigma Aldrich and was 99.99% pure (sublimed). The electrospray ionization mass spectrometry (ESI-MS) data were collected on an AB/Sciex QStar mass spectrometer with an ESI source, the electron impact mass spectrometry (EI-MS) data were collected on a Waters GC ToF mass spectrometer with an EI/CI source, and the DART-MS data were collected on a JEOL AccuTOF-DART mass spectrometer with a DART-ion source (no solvent is required). NMR spectra were recorded at ambient temperature and pressure using a Varian Gemini 400 MHz spectrometer (400 MHz for $^1$H, 100 MHz for $^{13}$C, and 161 MHz for $^{31}$P) unless stated otherwise. The $^1$H and $^{13}$C NMR spectra were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. All $^{31}$P chemical shifts were measured relative to 85% phosphoric acid as an external reference. Elemental analyses were performed at the Department of Chemistry, University of Toronto, on a Perkin-Elmer 2400 CHN elemental analyzer. Single-crystal X-ray diffraction data were collected using a Nonius Kappa CCD or Bruker Kappa APEX DUO diffractometer with Mo Kα radiation ($\lambda$ = 0.71073 Å). The CCD data were integrated and scaled using the *Denzo-SMN* package. The structures were solved and refined using *SHELXTL V6.1*. Refinement was by full-matrix least squares on $F^2$ using all data. Number-average molecular weights ($M_n$) and PDIs were measured by size-exclusion chromatography (SEC) using a Waters 1515 system equipped with a Waters 2707 autosampler, a Waters 2414 refractive index detector, and a Styragel HR 5E THF 7.8 × 300 mm column using tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with commercial polystyrene standards. Because of the structural differences between polycaprolactone (PCL) and polystyrene (PSt) units, we used a reported relationship to calculate the PCL molecular weights from PS-based SEC values ($M_{n,PCL} = 0.56M_{n,PSt}$).[86]


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**Synthesis of 1a ($C_{38}H_{33}O_3P_3$).** Diphenylphosphine oxide (1.186 g, 5.9 mmol) was dissolved in THF (5 mL) and added to a suspension of KH (0.235 g, 5.9 mmol) in THF (3 mL). Gas evolved, and the solution turned orange in color. After 30 min, gas evolution ceased and the solution was clear and orange. Bromoacetaldehyde diethyl acetal (0.677 g, 2.0 mmol) was added, and the solution turned less orange and cloudier over 15 min. The reaction was stirred overnight and turned milky orange in color. Water (20 mL) was added, and the solution was extracted with dichloromethane (DCM; 2 × 20 mL) and ether (2 × 20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure, and the white solid was washed with ether. Yield: 61.1% (0.753 g). Crystals of **1a** suitable for X-ray diffraction studies were grown from the slow evaporation of ether. $^1$H NMR (400 MHz, $CD_3Cl$): $\delta$ 7.82−7.75 (m, 4H, Ar−H), 7.71−7.63 (m, 4H, Ar−H), 7.35−7.13 (m, 22H, Ar−H), 4.75−4.59 (m, 1H, CH), 3.16−3.02 (m, 2H, $CH_2$). $^{31}$P NMR (161 MHz, $CD_3Cl$): $\delta$ 30.78 (d, $J$ = 14.1 Hz), 28.45 (t, $^3J_{PP}$ = 14.1 Hz). $^{13}$C NMR (100 MHz, $CD_3Cl$): $\delta$ 133.34 (d, Ar−C, $^1J_{CP}$ = 100.9 Hz), 131.96−131.68 (m, Ar−CH), 131.73 (dd, Ar−C, $^1J_{CP}$ = 100.8 Hz, $^4J_{CP}$ = 3.7 Hz), 131.55−131.39 (m, Ar−CH), 130.57 (d, Ar−CH, $J$ = 9.6 Hz), 128.62−128.19 (m, Ar−CH), 35.05 (td, CH, $J$ = 56.3 and 4.7 Hz), 24.24 (d, $CH_2$, $^1J_{CP}$ = 66.2 Hz). Anal. Calcd for $C_{38}H_{33}O_3P_3$: C, 72.38; H, 5.27. Found: C, 72.25; H, 5.65. MS (DART; $m/z^+$): 631.1 ($[C_{38}H_{34}O_3P_3]^+$).

**Synthesis of 1b ($C_{44}H_{45}O_3P_3$).** Similar to the synthesis of **1a**; see the Supporting Information, pages S2 and S3.

**Synthesis of 1c ($C_{44}H_{45}O_3P_3$).** Similar to the synthesis of **1a**; see the Supporting Information, pages S3 and S4.

**Synthesis of 1d ($C_{50}H_{57}O_3P_3$).** Similar to the synthesis of **1a**; see the Supporting Information, pages S4 and S5.

**Synthesis of 2a [$Y(NO_3)_3$(1a)].** **1a** (0.100 g, 0.16 mmol) was dissolved in $CH_3CN$ (4 mL). A solution of $[Y(H_2O)_6][NO]_3$ (0.061 g, 0.14 mmol) in $CH_3CN$ (1 mL) was added, and the mixture was stirred for 15 min. A white precipitate formed. The precipitate was filtered and washed with DCM (2 × 5 mL). Yield: 95.4% (0.137 g). Crystals suitable for X-ray diffraction studies were obtained from a 2:1 mixture of **1a** and $[Y(H_2O)_6][NO]_3$ in $CH_3CN$ diffused with ether. NMR spectra could not be obtained because **2a** was sparingly soluble in common NMR solvents other than DMSO-$d_6$, in which the DMSO displaced the phosphine oxide ligand. Anal. Calcd for $C_{38}H_{33}N_3O_{12}P_3Y$: C, 50.40; H, 3.67; N, 4.64. Found: C, 50.68; H, 3.71; N, 4.86. MS (DART; $m/z^+$): 631.2 ($[C_{38}H_{34}O_3P_3]^+$).

**Synthesis of 2b [$Y(NO_3)_3$(1b)].** Similar to the synthesis of **2a**; see the Supporting Information, page S5.

**Synthesis of 2c [$Y(NO_3)_3$(1c)].** Similar to the synthesis of **2a**; see the Supporting Information, page S6.

**Synthesis of 2d [$Y(NO_3)_3$(1d)].** Similar to the synthesis of **2a**; see the Supporting Information, page S6.

**Synthesis of 3a ($C_{38}H_{33}O_2P_3$).** The preparation of **3a** was conducted using a synthesis previously reported by Jenkins et al.[7S] **1a** (0.744 g, 1.18 mmol) was dissolved in 15 mL of DCM. The solution was cooled to 0 °C, and triflic anhydride (0.111 g, 0.393 mmol) was added. The solution turned pale yellow in color. After aging for 30 min, 1-pentanethiol (0.492 g, 4.72 mmol) and *N*,*N*-diisopropylethylamine (0.305 g, 2.36 mmol) were added. The solution quickly turned darker yellow in color. The solution was left for 16 h. The solution turned darker yellow in color. The reaction mixture was washed with a 5% $NaHCO_3$ solution (2 × 30 mL) and dried over anhydrous $Na_2SO_4$. The mixture was filtered, and the solvent was removed under reduced pressure. The crude yellow oil was dissolved in DCM and immobilized on a silica plug. The silica was washed with DCM and acetonitrile. The product was eluted with methanol, the solvent was removed under reduced pressure, and the yellow paste was recrystallized with cold ether and THF to yield a fine white powder. Yield: 48.3% (0.350 g). $^1$H NMR (400 MHz, $CD_3Cl$): $\delta$ 7.71−7.59 (m, 8H, Ar), 7.44−7.35 (m, 4H, Ar−H), 7.34−7.17 (m, 14H, Ar−H), 7.03−6.96 (m, 4H, Ar−H), 3.48−3.31 (m, 1H, CH), 2.58 (td, 2H, $CH_2$, $^1J_{HH}$ = 14.6 Hz, $^2J_{HP}$ = 6.9 Hz). $^{31}$P NMR (161 MHz, $CD_3Cl$): $\delta$ 30.44 (d, $^3J_{PP}$ = 13.3 Hz), −13.17 (t, $^3J_{PP}$ = 13.3 Hz). $^{13}$C NMR (100 MHz, $CD_3Cl$): $\delta$ 137.60 (d, C−P, $^1J_{CP}$ = 16.6 Hz), 132.06 (d, Ar−CH, $^2J_{CP}$ = 19.5 Hz), 132.25 (d, C−P, $^1J_{CP}$ = 17.9 Hz), 131.79 (s, Ar−CH), 131.70 (t, Ar−CH, $^2J_{CP}$ = 9.0 Hz), 131.56−131.46 (m, Ar−CH), 130.37 (d, C−P, $^1J_{PP}$ = 9.6 Hz), 128.82 (s, Ar−CH), 128.60 (s, Ar−CH), 128.53 (s, Ar−C), 128.44 (t, Ar−CH, $^2J_{CP}$ = 12.8 Hz), 40.31 (td, CH, $^1J_{CP}$ = 55.8 Hz, $^2J_{CP}$ = 14.0 Hz), 24.92 (d, $CH_2$, $^1J_{CP}$ = 21.4 Hz). Anal. Calcd for $C_{38}H_{33}O_2P_3 \cdot 0.5C_4H_{10}O$: C, 73.72; H, 5.41. Found: C, 73.98; H, 5.64. MS (DART; $m/z^+$): 615.2 ($[C_{38}H_{34}O_2P_3]^+$).

**Synthesis of 3b ($C_{44}H_{45}O_2P_3$).** Similar to the synthesis of **3a**; see the Supporting Information, pages S6 and S7.

**Synthesis of 3c ($C_{44}H_{45}O_2P_3$).** Similar to the synthesis of **3a**; see the Supporting Information, pages S7 and S8.

**Synthesis of 3d ($C_{44}H_{45}O_2P_3$).** Similar to the synthesis of **3a**; see the Supporting Information, pages S8 and S9.

**Synthesis of 4a [$Y(NO_3)_3(OPPh_3)$(3a)].** **3a** (0.100 g, 0.163 mmol) was dissolved in 3 mL of $CH_3CN$. A solution of $[Y(H_2O)_6][NO_3]_3$ (0.062 g, 0.163 mmol) in 1 mL of $CH_3CN$ was added. The mixture was allowed to stir for 5 min. A solution of triphenylphosphine oxide (0.045 g, 0.163 mmol) in 1 mL of $CH_3CN$ was added. The solution was removed under reduced pressure, and the white solid was washed with a 5:1 mixture of ether/DCM (5 mL). Yield: 66.8% (0.127 g). Crystals suitable for X-ray diffraction studies were obtained from a concentrated sample of **3a** in $CH_3CN$. $^1$H NMR (400 MHz, $CD_2Cl_2$, −20 °C): $\delta$ 7.68−7.09 (m, 38H, Ar−H), 6.83 (t, 6H, Ar−H, $^2J_{CP}$ = 7.4 Hz), 4.03−3.89 (m, 1H, CH), 2.51 (td, 2H, $CH_2$, $^1J_{CP}$ = 15.7 Hz, $^2J_{CP}$ = 6.2 Hz). Major product. $^{31}$P NMR (161 MHz, $CD_2Cl_2$, −20 °C): $\delta$ 39.79 (dd, $Ar_2PO$−CH, $^3J_{PP}$ = 11.2 Hz, $^2J_{YP}$ = 5.9 Hz, 36.5%), 35.72 (d, $OPPh_3$, $^2J_{YP}$ = 10.1 Hz, 21.5%), −14.05 (app t, $Ar_2P$−$CH_2$, 19.0%). Minor species in solution. $^{31}$P NMR (161 MHz, $CD_2Cl_2$, −20 °C): $\delta$ 41.40 (d, $^2J_{YP}$ = 7.9 Hz, 2.1%), 40.16 (dd, $^3J_{PP}$ = 11.6 Hz, $^2J_{YP}$ = 5.8 Hz, 2.1%), 39.40 (d, $^2J_{YP}$ = 5.7 Hz, 4.4%), 39.02 (dd, $^3J_{PP}$ = 13.9 Hz, $^2J_{YP}$ = 5.2 Hz, 1.4%), 38.13−37.78 (m, 0.7%), 37.55 (d, $^2J_{YP}$ = 10.9 Hz, 3.2%), 37.36 (d, $^2J_{YP}$ = 5.5 Hz, 1.4%), 36.69−36.56 (m, 3.5%), 35.18 (d, $^2J_{YP}$ = 9.4 Hz, 4.6%). $^{13}$C NMR (100 MHz, $CD_2Cl_2$, −20 °C): $\delta$ 136.15 (d, C−P, $^1J_{CP}$ = 14.3 Hz), 133.57 (s, Ar−CH), 133.48 (s, Ar−CH), 132.85 (s, Ar−CH), 132.64 (s, Ar−CH), 132.53−132.09 (m, Ar−CH), 131.40−131.1 (m, Ar−CH), 131.03−130.65 (m, Ar−CH), 129.47−128.26 (m, Ar−CH), 127.56 (d, C−P, $^1J_{CP}$ = 22.5 Hz), 124.17 (d, C−P, $^1J_{CP}$ = 104.5 Hz), 35.94 (td, CH, $^1J_{CP}$ = 53.6 Hz, $^3J_{CP}$ = 18.2 Hz), 23.62 (d, $CH_2$, $^1J_{CP}$ = 21.6 Hz). Anal. Calcd for $C_{56}H_{48}N_3O_{12}P_4Y \cdot 0.5CH_2Cl_2$: C, 56.07; H, 4.08; N, 3.47. Found: C, 56.08; H, 4.22; N, 3.78. MS (ESI; DCM; $m/z^+$): 615.2 ($[C_{38}H_{34}O_2P_3]^+$).

**Synthesis of 4b [$Y(NO_3)_3(OPPh_3)$(3b)].** Similar to the synthesis of **4a**; see the Supporting Information, pages S9 and S10.

**Synthesis of 4c [$Y(NO_3)_3(OPPh_3)$(3c)].** Similar to the synthesis of **4a**; see the Supporting Information, pages S10 and S11.

**Synthesis of 4d [$Y(NO_3)_3(OPPh_3)$(3d)].** Similar to the synthesis of **4a**; see the Supporting Information, pages S11 and S12.

**Polymerization Procedure.** Under a nitrogen atmosphere in a glovebox, a stock solution of 0.012 g of KO$^t$Bu in 10 mL of THF was prepared. A vial was charged with 0.0111 mmol of catalyst (0.010 g for **2a**, 0.011 g for **2b** or **2c**, and 0.012 g for **2d**) and 1 mL of the stock base solution and stirred for 5 min. A solution of 0.630 g of caprolactone (5.56 mmol) in 2.12 mL of THF was then added. The polymerization reaction was quenched with an excess of 1.0 M HCl and dried under vacuum to a constant weight.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Extended experimental section, crystal structure bond lengths and angles for **1a**−**1d**, **2a**−**2d**, and **4a**, crystallographic data tables for **1a**−**1d**, **2a**−**2d**, and **4a** (including CIF files), and ROP of $\varepsilon$-caprolactone using **2a**−**2d** and base. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) Byer, R. L. *Science* **1988**, *239*, 742−747.
(2) Lu, J.; Ueda, K.-I.; Yagi, H.; Yanagitani, T.; Akiyama, Y.; Kaminskii, A. A. *J. Alloys Compd.* **2002**, *341*, 220−225.
(3) Kinsman, K. M.; McKittrick, J.; Sluzky, E.; Hesse, K. *J. Am. Ceram. Soc.* **1994**, *77*, 2866−2872.
(4) Linares, R. C. *Solid State Commun.* **1964**, *2*, 229−231.
(5) Evans, W. J.; Sollberger, M. S. *Inorg. Chem.* **1988**, *27*, 4417−4423.
(6) Parker, D. *Chem. Soc. Rev.* **1990**, *19*, 271−291.
(7) Jang, Y. H.; Blanco, M.; Dasgupta, S.; Keire, D. A.; Shively, J. E.; Goddard, W. A. *J. Am. Chem. Soc.* **1999**, *121*, 6142−6151.
(8) Werner, M. E.; Karve, S.; Sukumar, R.; Cummings, N. D.; Copp, J. A.; Chen, R. C.; Zhang, T.; Wang, A. Z. *Biomaterials* **2011**, *32*, 8548−8554.
(9) Jankovic, D.; Vranjes-djuric, S.; Djokic, D.; Markovic, M.; Ajdinovic, B.; Jaukovic, L.; Nikolic, N. *J. Pharm. Sci.* **2012**, *101*, 2194−2203.
(10) Liu, Z.; Shi, J.; Jia, B.; Yu, Z.; Liu, Y.; Zhao, H.; Li, F.; Tian, J.; Chen, X.; Liu, S.; Wang, F. *Mol. Pharm.* **2011**, *8*, 591−599.
(11) Poorbaygi, H.; Aghamiri, S. M. R.; Sheibani, S.; Kamali-asl, A.; Mohagheghpoor, E. *Appl. Radiat. Isot.* **2011**, *69*, 1407−1414.
(12) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2001**, 637−638.
(13) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606−7607.
(14) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2002**, *103*, 283−316.
(15) Gromada, J. R. M.; Carpentier, J.-F.; Mortreux, A. *Coord. Chem. Rev.* **2004**, *248*, 397−410.
(16) Yasuda, H.; Ihara, E. *Tetrahedron* **1995**, *51*, 4563−4570.
(17) Kaneko, H.; Nagae, H.; Tsurugi, H.; Mashima, K. *J. Am. Chem. Soc.* **2011**, *133*, 19626−19629.
(18) Jian, Z.; Petrov, A. R.; Hangaly, N. K.; Li, S.; Rong, W.; Mou, Z.; Rufanov, K. A.; Harms, K.; Sundermeyer, J. R.; Cui, D. *Organometallics* **2012**, *31*, 4267−4282.
(19) Hannedouche, J.; Aillaud, I.; Collin, J.; Schulz, E.; Trifonov, A. *Chem. Commun.* **2008**, 3552−3554.
(20) Kim, J. Y.; Livinghouse, T. *Org. Lett.* **2005**, *7*, 1737−1739.
(21) Molander, G. A.; Knight, E. E. J. *Org. Chem.* **1998**, *63*, 7009−7012.
(22) Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415−4416.
(23) Evans, W. J.; Shreeve, J. L.; Doedens, R. J. *Inorg. Chem.* **1993**, *32*, 245−246.
(24) Cao, Y.; Du, Z.; Li, W.; Li, J.; Zhang, Y.; Xu, F.; Shen, Q. *Inorg. Chem.* **2011**, *50*, 3729−3737.
(25) Qian, C.; Zhu, D. *J. Chem. Soc., Dalton Trans.* **1994**, 1599−1603.
(26) Cao, T.-P.-A.; Buchard, A.; Le Goff, X. F.; Auffrant, A.; Williams, C. K. *Inorg. Chem.* **2012**, *51*, 2157−2169.
(27) Amgoune, A.; Thomas, C. M.; Carpentier, J.-F. *Macromol. Rapid Commun.* **2007**, *28*, 693−697.
(28) Alaaeddine, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Organometallics* **2009**, *28*, 1469−1475.
(29) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072−4073.
(30) Chamberlain, B. M.; Sun, Y.; Hagadorn, J. R.; Hemmesch, E. W.; Young, V. G.; Pink, M.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **1999**, *32*, 2400−2402.
(31) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *Macromol. Chem. Phys.* **2000**, *201*, 1329−1333.
(32) Löfgren, A.; Albertsson, A.-C.; Dubois, P.; Jérôme, R. *J. Macromol. Sci., Part C: Polym. Rev.* **1995**, *35*, 379−418.
(33) Li, X.; Zhu, Y.; Ling, J.; Shen, Z. *Macromol. Rapid Commun.* **2012**, *33*, 1008−1013.
(34) Li, G.; Lamberti, M.; Mazzeo, M.; Pappalardo, D.; Roviello, G.; Pellecchia, C. *Organometallics* **2012**, *31*, 1180−1188.
(35) Platel, R. H.; White, A. J. P.; Williams, C. K. *Inorg. Chem.* **2011**, *50*, 7718−7728.
(36) Broderick, E. M.; Guo, N.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Mehrkhodavandi, P.; Diaconescu, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 9278−9281.
(37) Tschan, M. J. L.; Brule, E.; Haquette, P.; Thomas, C. M. *Polym. Chem.* **2012**, *3*, 836−851.
(38) Carpentier, J.-F. *Angew. Chem., Int. Ed.* **2010**, *49*, 2662−2663.
(39) Williams, C. K.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 1−10.
(40) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11−63.
(41) Inkinen, S.; Hakkarainen, M.; Albertsson, A.-C.; Södergård, A. *Biomacromolecules* **2011**, *12*, 523−532.
(42) Dove, A. P. *Chem. Commun.* **2008**, 6446−6470.
(43) Vicente, G.; Zinner, L. G.; Rothschild, L. *Inorg. Chim. Acta* **1974**, *9*, 213−216.
(44) Vicentini, G.; Machado, L. C. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1676−1680.
(45) Zinner, L. B.; Vicentini, G.; Rothschild, L. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2499−2505.
(46) Vicentini, G.; Prado, J. C. *J. Inorg. Nucl. Chem.* **1972**, *34*, 1309−1317.
(47) Turanov, A. N.; Karandashev, V. K.; Baulin, V. E. *Solvent Extr. Ion Exch.* **2007**, *25*, 165−186.
(48) Turanov, A. N.; Karandashev, V. K.; Baulin, V. E.; Yarkevich, A. N.; Safronova, Z. V. *Solvent Extr. Ion Exch.* **2009**, *27*, 551−578.
(49) Nash, K. L.; Barrans, R. E.; Chiarizia, R.; Dietz, M. L.; Jensen, M. P.; Rickert, P. G.; Moyer, B. A.; Bonnesen, P. V.; Bryan, J. C.; Sachleben, R. A. *Solvent Extr. Ion Exch.* **2000**, *18*, 605−631.
(50) Eccles, H. *Solvent Extr. Ion Exch.* **2000**, *18*, 633−654.
(51) Nilsson, M.; Nash, K. L. *Solvent Extr. Ion Exch.* **2007**, *25*, 665−701.
(52) Dam, H. H.; Reinhoudt, D. N.; Verboom, W. *Chem. Soc. Rev.* **2007**, *36*, 367−377.
(53) Lumetta, G. J.; Gelis, A. V.; Vandegrift, G. F. *Solvent Extr. Ion Exch.* **2010**, *28*, 287−312.
(54) Mathur, J. N.; Murali, M. S.; Nash, K. L. *Solvent Extr. Ion Exch.* **2001**, *19*, 357−390.
(55) Berny, F.; Muzet, N.; Troxler, L.; Dedieu, A.; Wipff, G. *Inorg. Chem.* **1999**, *38*, 1244−1252.
(56) Boehme, C.; Wipff, G. *Inorg. Chem.* **2002**, *41*, 727−737.
(57) Coupez, B.; Boehme, C.; Wipff, G. *Phys. Chem. Chem. Phys.* **2002**, 457165729.
(58) Ward, T. M.; Allcox, I. L.; Wahl, G. H., Jr. *Tetrahedron Lett.* **1971**, *12*, 4421−4424.
(59) Baaden, M.; Berny, F.; Boehme, C.; Muzet, N.; Schurhammer, R.; Wipff, G. *J. Alloys Compd.* **2000**, *303*−*304*, 104−111.
(60) Sues, P. E.; Lough, A. J.; Morris, R. H. *Organometallics* **2011**, *30*, 4418−4431.
(61) Khachatryan, R. A. G.; Yu, N.; Indzhikyan, M. G. *Russ. J. Gen. Chem.* **1994**, *64*, 1134−1138.
(62) Kabachnik, M. I.; Medved, T. Y.; Polikarpov, Y. M.; Yudina, K. S. *Russ. Chem. Bull.* **1967**, *16*, 568−572.
(63) Zhang, J.; Li, A.; Hor, T. S. A. *Dalton Trans.* **2009**, 9327−9333.
(64) Zhang, J.; Braunstein, P.; Hor, T. S. A. *Organometallics* **2008**, *27*, 4277−4279.
(65) Reger, D. L.; Semeniuc, R. F.; Gardinier, J. R.; O'Neal, J.; Reinecke, B.; Smith, M. D. *Inorg. Chem.* **2006**, *45*, 4337−4339.
(66) Reger, D. L.; Elgin, J. D.; Semeniuc, R. F.; Pellechia, P. J.; Smith, M. D. *Chem. Commun.* **2005**, 4068−4070.
(67) Lopez Aparicio, F. J.; Zorrilla Benitez, F. J.; Alvarez-Manzaneda Roldan, E. J. *An. Quim., Ser. C* **1988**, *84*, 277−284.

(68) Yavari, I.; Hadigheh-Rezvan, V. *Phosphorus, Sulfur, Silicon Relat. Elem.* **2001**, *174*, 151−162.
(69) Popovici, C.; Fernandez, I.; Ona-Burgos, P.; Roces, L.; Garcia-Granda, S.; Ortiz, F. L. *Dalton Trans.* **2011**, *40*, 6691−6703.
(70) Ge, Y. W.; Sharp, P. R. *Inorg. Chem.* **1992**, *31*, 379−384.
(71) Ye, C.; Sharp, P. R. *Inorg. Chem.* **1995**, *34*, 55−59.
(72) Wells, K. D.; McDonald, R.; Ferguson, M. J.; Cowie, M. *Inorg. Chem.* **2011**, *50*, 3523−3538.
(73) Sharp, P. R.; Ge, Y. W. *J. Am. Chem. Soc.* **1987**, *109*, 3796−3797.
(74) Ge, Y. W.; Sharp, P. R. *Organometallics* **1988**, *7*, 2234−2236.
(75) Petersson, M. J.; Loughlin, W. A.; Jenkins, I. D. *Chem. Commun.* **2008**, 4493−4494.
(76) Zhang, W.-H.; Chien, S. W.; Hor, T. S. A. *Coord. Chem. Rev.* **2011**, *255*, 1991−2024.
(77) Deakin, L.; Levason, W.; Popham, M. C.; Reid, G.; Webster, M. *J. Chem. Soc., Dalton Trans.* **2000**, 2439−2447.
(78) Hill, N. J.; Levason, W.; Popham, M. C.; Reid, G.; Webster, M. *Polyhedron* **2002**, *21*, 445−455.
(79) Kalck, P.; Serra, C.; Machet, C.; Broussier, R.; Gautheron, B.; Delmas, G.; Trouve, G.; Kubicki, M. *Organometallics* **1993**, *12*, 1021−1022.
(80) Oishi, M.; Kato, T.; Nakagawa, M.; Suzuki, H. *Organometallics* **2008**, *27*, 6046−6049.
(81) Baranger, A. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7890−7891.
(82) Cornelissen, C.; Erker, G.; Kehr, G.; Fröhlich, R. *Organometallics* **2004**, *24*, 214−225.
(83) Ozawa, F.; Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Henling, L. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1319−1327.
(84) Ferguson, G. S.; Wolczanski, P. T.; Parkanyi, L.; Zonnevylle, M. C. *Organometallics* **1988**, *7*, 1967−1979.
(85) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889−899.
(86) Ling, J.; Liu, J.; Shen, Z.; Hogen-Esch, T. E. *J. Polym. Sci. A, Polym. Chem.* **2011**, *49*, 2081−2089.
(87) Stevels, W. M.; Ankoné, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 8296−8303.
(88) Martin, E.; Dubois, P.; Jérôme, R. *Macromolecules* **2000**, *33*, 1530−1535.
(89) Gou, P.; Zhu, W.; Shen, Z. *Front. Chem. Eng. China* **2008**, *3*, 330−337.
(90) Wang, Y.; Onozawa, S.-Y.; Kunioka, M. *Green Chem.* **2003**, *5*, 571−574.
(91) Susperregui, N.; Kramer, M. U.; Okuda, J.; Maron, L. *Organometallics* **2011**, *30*, 1326−1333.
(92) Wang, L.; Cui, D.; Hou, Z.; Li, W.; Li, Y. *Organometallics* **2011**, *30*, 760−767.
(93) Jenter, J.; Roesky, P. W.; Ajellal, N.; Guillaume, S. M.; Susperregui, N.; Maron, L. *Chem.—Eur. J.* **2010**, *16*, 4629−4638.
(94) Ni, X.; Liang, Z.; Ling, J.; Li, X.; Shen, Z. *Polym. Int.* **2011**, *60*, 1745−1752.
(95) Ito, K.; Hashizuka, Y.; Yamashita, Y. *Macromolecules* **1977**, *10*, 821−824.
(96) Gitsov, I.; Ivanova, P. T.; Fréchet, J. M. J. *Macromol. Rapid Commun.* **1994**, *15*, 387−393.
(97) Stridsberg, K.; Ryner, M.; Albertsson, A.-C. *Adv. Polym. Sci.* **2002**, *157*, 41−65.