

## CMPO-Functionalized $C_3$ -Symmetric Tripodal Ligands in Liquid/Liquid Extractions: Efficient, Selective Recognition of Pu(IV) with Low Affinity for $3+$ Metal Ions

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Structural modifications of carbamoylmethylphosphine oxide (CPMO)-functionalized triphenoxymethane platforms are described, and the influence of these changes on the ability of the ligand to extract actinides from simulated acidic nuclear waste streams has been evaluated. The ligand system has been shown to have excellent binding efficiency and a selectivity for An(IV) in comparison to the a simple monomeric CMPO ligand under analogous conditions. Both the extraction efficiency and selectivity are strongly dependent on the flexibility and electronic properties of the ligating units in the triphenoxymethane construct. The Tb(III) and Bi(III) nitrate complexes of tris-CMPO derivatives have been isolated, and their structures were elucidated by NMR, ESI FT-ICR MS, and X-ray analysis, providing information on the interactions between metal ions and the tris-CMPO molecules.

### Introduction

In a typical light-water reactor, the operational life-span of a fuel rod is only 3 years, yet they still contain some energy potential. The recycling of fuel rods potentially offers both significant economic and environmental impacts.<sup>1</sup> The scale of the waste problem is truly impressive, given that nuclear reactors in the U.S. annually produce 98 GW of power.<sup>2</sup> A single 1 GW reactor will produce approximately 30 tonnes of spent fuel each year, and depending on the burnup and cooling time of the rods, there will be approximately 0.2 tonnes of <sup>239</sup>Pu and 0.02 tonnes of the minor actinides (neptunium, americium, and curium) produced as waste.<sup>3</sup> In the U.S., spent fuel rods currently remain in storage at the reactor, awaiting transport for disposal at a government repository. Protracted litigation, however, may keep the Yucca Mountain Repository closed for many years.<sup>4</sup> The partitioning of radioactive waste followed by the transmuta-

tion of problematic long-lived radionuclides would reduce uncertainties related to the long-term waste storage (several hundred thousand years) in the geological repositories. In addition, the development of safe recycling and disposal technologies will help raise public awareness and acceptability of nuclear power as the most viable energy source to sustain global development without significant environmental consequences.

After removal from a reactor, a spent rod is still predominately made up of <sup>238</sup>U, but the rod contains some useful amounts <sup>235</sup>U and <sup>239</sup>Pu. The remaining 3–4% of the fuel has been converted primarily to a mixture of radioactive and nonradioactive fission products. Although no definitive procedures have been set by the Department of Energy, several options have been proposed. One possible protocol for spent fuel reprocessing would involve the recovery of the two major components (uranium and plutonium), followed by the separation of long-lived transplutonium radionuclides from the other elements. Uranium and plutonium could then be converted back to fuel, whereas the long-lived actinides could be transmuted into short-lived and nonradioactive elements thus decreasing the volume and long-term radiotoxicity of the waste. Unfortunately, the transm-

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tation of actinides would be impeded by even small amounts of lanthanide ions due to the large neutron capture cross sections of these elements, and an efficient protocol for their separation must be developed for this process to work.

The solvent extraction separation process used in waste reprocessing is based on the transfer of a metal cation from an acidic aqueous phase into an immiscible organic phase with simultaneous charge neutralization.<sup>5,6</sup> During the extraction, a variety of species are formed in the combination of ionic metals with water, acid, and organic solvent. The extent of the extraction can be expressed by the distribution ratio ( $D = \frac{\sum[M_{\text{org}}]}{\sum[M_{\text{aq}}]}$ ) of the total metal ion concentration in the organic phase ( $\sum[M_{\text{org}}]$ ) against the total metal ion concentration in the aqueous phase ( $\sum[M_{\text{aq}}]$ ), or percentage wise (%E =  $100\% \left( \frac{[M^{n+}]_{\text{org}}}{[M^{n+}]_{\text{total}}} \right)$ ). In the liquid-liquid extraction process, the extractant is commonly diluted/dissolved in a water immiscible organic solvent. Therefore, successful and efficient separation is determined not only by the choice of the proper ligand, but also by the careful selection of the organic solvent and the content of the aqueous solution.

Nuclear waste reprocessing begins with the dissolution of used fuel rods or waste in concentrated nitric acid. To date, the most successful technique used for the partitioning of nuclear waste components predominately employs organophosphorus extractants. Industrial uranium and plutonium recovery utilizes neutral monodentate tri-*n*-butyl phosphate (TBP) (**1**) in the PUREX (Plutonium/URanium EXtraction) process.<sup>7,8</sup> Other popular organophosphorus compounds like bidentate octyl(phenyl)-*N,N*-diisobutylcarbamoyl methylphosphine oxide (CMPO) (**2**) and dihexyl-*N,N*-diethylcarbamoylmethylene phosphonate (DHDECMP) (**3**)<sup>9</sup> are widely studied as chelating agents for both actinides and lanthanides. The mixture of CMPO and TBP extractants, originally studied by Horwitz and co-workers, is applied in the commercially operating TRUEX (TRAnSUrnic elements EXtraction) process<sup>10–12</sup> for removal of both lanthanide and actinide ions from high-level liquid waste generated during PUREX reprocessing.<sup>13–15</sup> The TRUEX process generates a great deal of nonincinerable, phosphorus-containing waste

(1.4 M TBP and 0.2 M CMPO),<sup>12</sup> and to reduce the volume of the secondary waste produced by TRUEX, development of either a completely incinerable (CHON-based) or a more efficient phosphorus-based extraction system is highly desirable. Although the PUREX process for the separation of Pu(IV) is inexpensive, efficient, and highly refined, the waste reprocessing remains a difficult and important problem, particularly in the case of Am(III) and Cm(III). The continued development of new ligand types that are highly efficient and selective for any of the actinides including Pu(IV) may be of aid in the eventual solution of the most difficult separation problems faced in nuclear waste recycling.

The chemical properties of lanthanides and actinide are similar, and historically, the close relationship between the two groups of elements helped predict the properties of the transplutonium elements, facilitating their eventual synthesis and isolation. From a waste reprocessing perspective, such similarities are disadvantageous. The matching oxidation states of trivalent actinides and lanthanides and an approximately equal ionic radii make the separation particularly difficult. Both An(III) and Ln(III) are hard acids and form complexes preferentially with hard bases through strong ionic interactions. A careful examination of their electronic structures and binding with less-compatible soft bases revealed that small but important differences between these two groups of cations are evident.<sup>16</sup>

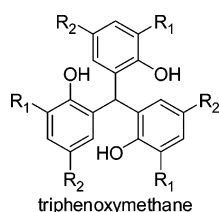
The exceptional stability of the lanthanides' trivalent oxidation state is perhaps the most exceptional difference between the two groups.<sup>16</sup> Across the lanthanide series, the radii of the outer 6s and 5d orbitals are significantly larger than the average radius of the 4f orbital, which effectively shields the f electrons and stabilizes the third oxidation state.<sup>17</sup> In the case of actinides, more spatially extended 5f orbitals are no longer effectively shielded by the outer 7s and 6d orbitals, resulting in the decreased stability of the trivalent state. The later actinides (transplutonium elements) show somewhat higher stability of the third oxidation state with respect to the early members of the group due to the slight decrease in the size of the 5f orbital radius with respect to the size of 7s and 6d orbitals as the elements become heavier. This effect provides some shielding of f orbitals, although it is not as effective as in the case of the 4f orbitals of lanthanides.<sup>16,18</sup>

For liquid/liquid extractions, the binding efficiency and/or selectivity of ligands for lanthanides and actinides can be significantly improved by the preorganization of several ligating units on a molecular platform. Particularly interesting are cases of CMPO moieties secured to a variety of calix[4]arene and resorcinarene platforms<sup>19–25</sup> or tripo-

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dands such as 1,1,1-tris[(aminopropoxy)methyl]propane and 1,3,5-trialkylbenzene.<sup>26,27</sup> Previously, we have reported the synthesis of a modified chelate system with three precisely arranged carbamoylmethylphosphine oxide moieties attached to a rigid, triphenoxymethane platform (tris-CMPO),<sup>28</sup> and Böhmer and co-workers have produced a related molecule built on the opposite side of the triphenoxymethane platform.<sup>29</sup> The extraction activities of our triphenoxymethane ligand for a selected group of trivalent lanthanides and tetravalent thorium have been compared to multi-CMPO calix[4]arene-based extractant as well as the commercial CMPO ligand under similar conditions of concentration and solvent. The impact of further structural ligand derivatization on the extraction selectivity and efficiency for tetravalent actinides, in particular plutonium, is presented herein. The extraction behavior of the tris-CMPO derivatives in comparison to the classical CMPO and other multi-CMPO systems has been discussed, demonstrating an overall improvement in the development of CMPO-based extractants for actinide/lanthanide separations.



In addition, metal complexes of tris-CMPO derivatives have been isolated, and their structures were elucidated by NMR, ICR-MS, and X-ray analysis, which provided potential rationalization for the presented ligands' extraction behavior.

## Experimental Section

**General Considerations.** The lanthanide and actinide salts, La(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O (Alpha Aesar), Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Eu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (Aldrich), Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (Acros), and Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O (Strem), were used as received. The solutions were prepared from 18 MΩ Millipore

deionized water, TraceMetal-grade HNO<sub>3</sub> (Fisher Scientific), and HPLC-grade organic solvents. The Arsenazo(III) assay was performed on a Varian Cary 50 UV-vis spectrophotometer, whereas a 2500TR Packard liquid scintillation analyzer was used for counting α-emitting plutonium and uranium radionuclides. A Canberra GammaTrac 1185 with a germanium detector and an AccuSpec-B multichannel analyzer was used for <sup>241</sup>Am and <sup>152</sup>Eu counting. All of the <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on a Varian VXR-300 or Mercury-300 spectrometer at 299.95 and 121.42 MHz for the proton and phosphorus channels, respectively. Elemental analyses were performed by Complete Analysis Laboratories, Inc., in Passipany, New Jersey. Mass spectrometry samples were analyzed by Dr. Lidia Matveeva and Dr. Dave Powell at the University of Florida on a Bruker Apex II 4.7 T Fourier transform ion cyclotron resonance mass spectrometer. Fast atom bombardment (FAB), ionization energy (IE), and liquid secondary ion mass spectrometry (LSIMS) mass spectra were recorded on a Finnigan MAT95Q Hybrid Sector.

**Metal Ion Extractions.** The lanthanides, bismuth, and thorium extraction experiments followed a previously reported procedure.<sup>21,28,30</sup> The extractability of each cation was calculated as %E = 100/(A<sub>1</sub> - A)/(A<sub>1</sub> - A<sub>0</sub>), where A is the absorbance of the extracted aqueous phase with the Arsenazo(III) indicator, A<sub>1</sub> is the absorbance of the aqueous phase before extraction with the indicator, and A<sub>0</sub> is the absorbance of metal-free 1 M nitric acid and the indicator (λ<sub>Ln(III)</sub> = 655, λ<sub>Bi(III), Th(IV)</sub> = 665 nm).

In the case of <sup>239</sup>Pu, <sup>238</sup>U, <sup>241</sup>Am, and <sup>152</sup>Eu isotopes, a solution of ligand, 10<sup>-3</sup> to 10<sup>-2</sup> M in CH<sub>2</sub>Cl<sub>2</sub>, or 1-octanol has been contacted with 1 M HNO<sub>3</sub>-containing radioactive nuclides. The acid concentrations were measured by titration with phenylphthalein and give the low concentrations of both extractants and metals; no significant HNO<sub>3</sub> coextraction should occur with dichloromethane. Test tubes containing 1–2 mL of the aqueous phase and an equal volume of the organic phase were placed into an orbital shaker at 20 °C for 20–24 h to allow the system to reach equilibrium. The test tubes were removed from the rotator, the layers were allowed to separate, and then were transferred into the shell vials. Equal aliquots of the organic and the aqueous phases were taken for counting and distribution coefficient determination.

**Isotopes Stock Solutions. Plutonium Stock Solution.** The stock solution of tetravalent <sup>239</sup>Pu was purified using the anion exchange method.<sup>31</sup> The method is based on the retention of Pu(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup> in 7.5 M HNO<sub>3</sub> by the anion exchanger (Bio-Rad AG-1 × 8). All of the cations were eluted from the column with 7.5 M HNO<sub>3</sub>. Subsequently, plutonium was stripped from the column with a solution of 0.3 M HNO<sub>3</sub> at 60 °C. The strip was taken to a wet salt with a few drops of concentrated HClO<sub>4</sub> to destroy any organic impurities. The resulting Pu(VI) salt was dissolved in 1 M HNO<sub>3</sub> and was treated with 0.1 mL of concentrated H<sub>2</sub>O<sub>2</sub> to convert plutonium to tri- and tetravalent oxidation states.<sup>31</sup> To oxidize Pu(III) to Pu(IV), 20 mg of solid NaNO<sub>2</sub> was added to the solution. An electron absorption spectrum, collected in 400–900 nm range, revealed no evidence of either Pu(III) or Pu(VI). The solution was diluted with 1 M HNO<sub>3</sub> to get 10<sup>-5</sup> M Pu(IV) and was used for the experiments.

**Uranium Stock Solution.** A weighted amount of <sup>238</sup>U<sub>3</sub>O<sub>8</sub> of analytical purity was dissolved in 14.7 M HNO<sub>3</sub> and then diluted with water to 1.6 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> in 1 M HNO<sub>3</sub>. The solution was then diluted with 1 M HNO<sub>3</sub> to 0.01 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> and was spiked

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with  $^{233}\text{U(VI)}$  ( $T_{1/2} = 1.59 \times 10^5$  y) to increase the effectiveness of the liquid scintillation counting.

**Americium and Europium Stock Solutions.** The purity of the  $^{241}\text{Am}$  stock solution was determined by the ICPMS analysis. The solution was evaporated to dryness and redissolved in 1 M  $\text{HNO}_3$ . The  $^{152}\text{Eu}$  stock was purchased from Isotope Products Laboratories. The original 0.5 M  $\text{HCl}$  solution was taken to a wet salt with nitric acid twice and was then redissolved in 1 M  $\text{HNO}_3$ . The activities of the stock solutions were 1 micro Ci per 1 mL. The working solutions were spiked with the gamma nuclides with amounts to provide good counting statistics for each sample within  $\sim 1\%$  error.

**Synthesis.** The synthetic methodology for the preparation of **8** and **12** has been adapted from procedures developed in work with phenols and calix[*n*]arene platforms.<sup>19,32</sup> Detailed synthetic procedures were previously reported for the preparation of **8b**.<sup>28,33,34</sup>

**Tris(3,5-*tert*-pentyl-2-(cyanomethoxy)phenyl)methane, 5a.** Following the procedure described in ref 19 for **5b**, a 10.70 g portion (15.00 mmol) of **4a** was dissolved in dry acetone (200 mL) with 20.73 g (150.00 mmol) of potassium carbonate, 22.48 g (150.00 mmol) of sodium iodide, and 7.59 g (120.00 mmol) of chloroacetonitrile, and the solution was refluxed for 48 h under nitrogen. After the solvent was removed in vacuo, the product was taken up in ether, dried with  $\text{MgSO}_4$ , filtered, and the solvent was removed. Recrystallization of the crude material from ethanol afforded 8.91 g (72%) of product.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 0.55$  (m, 18 H;  $\text{CH}_2\text{CH}_3$ ), 1.13 (s, 18 H; C- $\text{CH}_3$ ), 1.36 (s, 18 H; C- $\text{CH}_3$ ), 1.48 (q,  $J = 7.4$ , 6 H;  $\text{CH}_2\text{CH}_3$ ), 1.74 (q,  $J = 7.5$ , 6 H;  $\text{CH}_2\text{CH}_3$ ), 4.14 (s, 6H;  $\text{CH}_2\text{CN}$ ), 6.17 (s, 1 H; CH), 7.04 (d,  $J = 2.6$ , 3 H; Ar- $H$ ), 7.15 (d,  $J = 2.3$ , 3 H; Ar- $H$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 9.4$ , 9.7, 28.6, 29.4, 35.5, 37.0, 38.1, 38.5, 39.5, (aliphatic); 57.8 (Ar-O- $\text{CH}_2$ ); 115.0 (CN); 126.3, 127.5, 136.0, 141.5, 145.7, 151.8 (aromatic). Anal. Calcd for  $\text{C}_{55}\text{H}_{79}\text{N}_3\text{O}_3$ : C, 79.57; H, 9.59; N, 5.06. Found: C, 79.75; H, 10.07; N, 4.96.

**Tris(3-methyl-5-*tert*-butyl-2-(cyanomethoxy)phenyl)methane, 5c.** Following the procedure described above, a 0.55 g (1.1 mmol) portion of **4c** yielded 0.59 g (89%) of pure product.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 1.18$  (s, 27 H; Ar- $\text{C}(\text{CH}_3)_3$ ), 2.37 (s, 9 H; Ar- $\text{CH}_3$ ), 4.14 (s, 6H; Ar-O- $\text{CH}_2\text{CN}$ ), 6.22 (s, 1 H; C- $H$ ), 6.85 (b, 3 H; Ar- $H$ ), 7.12 (d, 3 H; Ar- $H$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 17.1$ , 31.2, 34.3, 37.7, 57.2 (aliphatic); 115.5 (CN); 125.5, 127.4, 130.9, 135.0, 147.9, 151.4 (aromatic). Anal. Calcd for  $\text{C}_{40}\text{H}_{49}\text{N}_3\text{O}_3$ : C, 77.51; H, 7.97; N, 6.78. Found: C, 77.68; H, 8.36; N, 6.71.

**1,1'-bis(3,5-di-*tert*-butyl-2-(cyanomethoxy)phenyl)ethane.** As described for **5a**, a 6.57 g (14.98 mmol) portion of 2,2'-ethylidenebis(4,6-di-*tert*-butylphenol) to afford 4.20 g (54%) of product.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 1.18$  (s, 18 H;  $\text{CCH}_3$ ), 1.34 (s, 18 H;  $\text{CCH}_3$ ), 1.60 (d,  $J = 6.9$ , 3 H;  $\text{CHCH}_3$ ), 4.52 (m, 4 H;  $\text{CH}_2\text{CN}$ ), 4.65 (q,  $J = 7.1$ , 1 H;  $\text{CHCH}_3$ ), 7.11 (d,  $J = 2.6$ , 2 H; Ar- $H$ ), 7.18 (d,  $J = 2.6$ , 2 H; Ar- $H$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 23.3$ , 31.6, 31.7, 32.3, 34.9, 35.7, (aliphatic); 58.9 (Ar-O- $\text{CH}_2$ ), 115.7 (CN); 123.4, 124.2, 138.4, 142.5, 147.7, 152.2, (aromatic). Anal. Calcd for  $\text{C}_{34}\text{H}_{48}\text{N}_2\text{O}_2$ : C, 79.02; H, 9.36; N, 5.42. Found: C, 79.39; H, 9.82; N, 5.44.

**Tris(3,5-di-*tert*-pentyl-2-(aminomethoxy)phenyl)methane, 6a.** As outlined in ref 19, a diethyl ether solution of **5a** (7.12 g, 8.58 mmol) was added dropwise over 30 min to a slurry of lithium

aluminum hydride (4.36 g, 129.00 mmol) in diethyl ether at 0 °C. The mixture was allowed to warm to room temperature and stirred for an additional 12–15 h. A 10 mL portion of 5%  $\text{NaOH}$  was slowly added to the slurry, and the solution was allowed to stir for 30 min. The solution was dried with  $\text{MgSO}_4$ , filtered, and the solvent was removed in vacuo. The crude white solid was recrystallized from acetonitrile to give to give 6.00 g (83%) of product.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 0.48$  (m, 18 H;  $\text{CH}_2\text{CH}_3$ ), 1.11 (s, 18 H;  $\text{CCH}_3$ ), 1.30 (s, 18 H;  $\text{CCH}_3$ ), 1.43 (q,  $J = 7.4$ , 6 H;  $\text{CH}_2\text{CH}_3$ ), 1.67 (q,  $J = 7.4$ , 6 H;  $\text{CH}_2\text{CH}_3$ ), 2.89 (t,  $J = 5.0$ , 6 H;  $\text{CH}_2\text{CH}_2\text{-NH}_2$ ), 3.32 (t,  $J = 5.0$ , 6 H; O- $\text{CH}_2\text{CH}_2$ ), 6.38 (s, 1 H; CH), 7.00 (d,  $J = 2.6$ , 3 H; Ar- $H$ ), 7.12 (d,  $J = 2.3$ , 3 H; Ar- $H$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 9.3$ , 9.8, 28.8, 29.7, 35.3, 37.1, 37.9, 38.8, 39.4 (aliphatic); 42.8 ( $\text{CH}_2\text{-NH}_2$ ); 74.4 (O- $\text{CH}_2$ ); 125.0, 128.2, 138.0, 140.1, 142.8, 152.9 (aromatic). Anal. Calcd for  $\text{C}_{55}\text{H}_{91}\text{N}_3\text{O}_3$ : C, 78.42; H, 10.89; N, 4.99. Found: C, 78.13; H, 11.35; N, 4.66.

**Tris(3-methyl-5-*tert*-butyl-2-(aminomethoxy)phenyl)methane, 6c.** Following the procedure outlined for **6a**, a 6.46 g (10.0 mmol) portion of **5c** gave 5.7 g (86%) of product.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 1.18$  (s, 27 H; Ar- $\text{C}(\text{CH}_3)_3$ ), 2.26 (s, 9 H; Ar- $\text{CH}_3$ ), 2.87 (t,  $J = 5.1$  Hz, 6 H; Ar-O- $\text{CH}_2$ ), 3.31 (t,  $J = 5.2$  Hz, 6 H; Ar-O- $\text{CH}_2\text{CH}_2\text{NH}_2$ ), 6.76 (s, 1 H; CH), 6.92 (d,  $J = 2.6$  Hz, 3 H; Ar- $H$ ), 7.00 (d,  $J = 2.6$  Hz, 3 H; Ar- $H$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 16.8$ , 31.3, 34.1, 36.9, 42.4, 74.2 (aliphatic); 125.8, 125.9, 129.8, 136.3, 145.5, 152.3 (aromatic); LSI MS [ $\text{M}+\text{H}$ ] $^+$  = 632.48.

**1,1'-bis(3,5-di-*tert*-butyl-2-(2-aminoethoxy)phenyl)ethane.** Lithium aluminum hydride (1.49 g, 39.26 mmol) was suspended in dry ether (80 mL), and the reaction flask was cooled to 0 °C. 1,1'-bis(3,5-di-*tert*-butyl-2-(cyanomethoxy)phenyl)ethane (2.70 g, 5.23 mmol) was added in three portions with stirring. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was monitored by TLC. (pentane/ether 80:20) and once completed, 5% sodium hydroxide solution (4.5 mL) was added dropwise (ice bath) and the mixture was stirred until the suspension became milky white. The resulting white solid was discarded through filtration, and the organic layer was dried over  $\text{MgSO}_4$ . Removal of the solvent under vacuum yielded analytically pure product. Yield 2.30 g (84%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 1.27$  (s, 18 H,  $\text{CH}_3$ ), 1.42 (s, 18 H,  $\text{CH}_3$ ), 1.67 (d, 3 H,  $J = 7.2$  Hz,  $\text{CHCH}_3$ ), 3.15 (b t, 4 H, N- $\text{CH}_2\text{-CH}_2\text{-O}$ ), 3.89 (m, 4 H, N- $\text{CH}_2\text{CH}_2\text{-O}$ ), 4.70 (q, 1 H,  $J = 7.2$  Hz, CH), 7.21 (s, 2 H, Ar- $H$ ), 7.24 (s, 2 H, Ar- $H$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 23.95$ , 30.18, 31.57, 31.69, 32.33, 34.70, 35.64, 42.52 (aliphatic); 75.62 (O- $\text{CH}_2$ ); 122.54, 124.69, 139.02, 141.80, 145.18, 153.66 (aromatic). Anal. Calcd for  $\text{C}_{34}\text{H}_{56}\text{N}_2\text{O}_2$ : C, 77.81; H, 10.76; N, 5.34. Found: C, 78.32; H, 11.14; N, 5.08

**Preparation of 8a.** The synthesis of **8a** followed the preparation method for **8b**.<sup>28</sup> A chloroform solution of **6a** (2.92 g, 3.47 mmol) and *p*-nitrophenyl(diphenylphosphoryl)acetate, **7**, (4.16 g, 10.91 mmol) were stirred at 45 °C for 3 days. After cooling to room temperature, a 1 M solution of  $\text{NaOH}$  (100 mL) was added and the mixture was stirred for 2 h. The *p*-nitrophenol sodium salt was extracted from the chloroform solution using 5% sodium carbonate (6  $\times$  300 mL), and the organic layer was further extracted with brine. The organic phase was dried with  $\text{MgSO}_4$ , filtered, and the solvent was removed in vacuo to give 4.21 g (77%) of product as an off-white solid material.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 0.46$  (m, 18 H;  $\text{CH}_2\text{CH}_3$ ), 1.06 (s, 18 H;  $\text{CCH}_3$ ), 1.23 (s, 18 H;  $\text{CCH}_3$ ), 1.40 (q,  $J = 7.3$ , 6 H;  $\text{CH}_2\text{CH}_3$ ), 1.57 (b, 6 H;  $\text{CH}_2\text{CH}_3$ ), 3.41 (b, m, 18 H; O- $\text{CH}_2\text{CH}_2\text{-NHC(O)-CH}_2\text{-P}$ ), 6.28 (s, 1 H; CH), 6.92 (d,  $J = 2.3$ , 3 H; Ar- $H$ ), 6.95 (d,  $J = 2.1$ , 3 H; Ar- $H$ ), 7.38 (m, 18 H; P-Ar  $H$ ), 7.72 (m, 12 H; P-Ar  $H$ ), 7.89 (b, 3 H; NH).  $^{13}\text{C NMR}$

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(CDCl<sub>3</sub>):  $\delta$  = 9.3, 9.8, 28.7, 29.7, 35.5, 37.1, 37.8, 38.7, 39.3, 39.5 (aliphatic); 40.4 (CH<sub>2</sub>-NH<sub>2</sub>); 70.4 (O-CH<sub>2</sub>); 125.0, 127.7, 128.7, 128.9, 131.2, 131.3, 132.1, 132.2, 137.8, 139.9, 142.8, 153.2 (aromatic); 165.4; 165.5 (C=O). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  = 29.8. Anal. Calcd for C<sub>97</sub>H<sub>124</sub>N<sub>3</sub>O<sub>9</sub>P<sub>3</sub>: C, 74.26; H, 7.97; N, 2.68. Found: C, 74.59; H, 8.14; N, 2.70.

**Preparation of 8c.** Following the procedure described above for **8a**, a 2.60 g (4.11 mmol) portion of **6c** was reacted with 4.90 g (12.85 mmol) of **7** to afford 1.97 g (35%) of product. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.14 (s, 27 H; Ar-C(CH<sub>3</sub>)<sub>3</sub>), 2.12 (s, 9 H; Ar-CH<sub>3</sub>), 3.29 (b, 12 H; Ar-O-CH<sub>2</sub>CH<sub>2</sub>), 3.49 (d,  $J$ (H,P) = 13.9 Hz, 6 H; CH<sub>2</sub>-POAr<sub>2</sub>), 6.65 (s, 1 H; CH), 6.84 (d,  $J$  = 2.4 Hz, 3 H; Ar-H), 6.94 (d,  $J$  = 2.5 Hz, 3 H; Ar-H), 7.38 (m, 12 H; P-Ar H), 7.47 (m, 6 H; P-Ar H), 7.76 (m, 12 H; P-Ar H), 8.00 (b, 3 H; N-H). <sup>13</sup>C NMR [CDCl<sub>3</sub>]:  $\delta$  = 16.79, 31.2, 34.0, 38.7, 39.5, 40.0 (aliphatic); 70.6 (O-CH<sub>2</sub>); 152.1, 145.6, 135.9, 132.7, 131.9, 131.4, 131.0, 130.9, 129.7, 128.6, 128.4, 126.0, 125.5 (aromatic); 165.1, 165.09 (C=O). <sup>31</sup>P NMR (CD<sub>3</sub>OD):  $\delta$  = 30.77. HR ESI-ICR MS (sample injected as solution in 1% HNO<sub>3</sub>/MeOH): [M+H]<sup>+</sup> = 1358.62. Anal. Calcd for C<sub>82</sub>H<sub>94</sub>N<sub>3</sub>O<sub>9</sub>P<sub>3</sub>: C, 72.49; H, 6.97; N, 3.09. Found: C, 72.37; H, 6.97; N, 3.38.

**Preparation of 9.** The synthesis of **9** was adapted from that described above for **8a**, and a 1.15 g (2.19 mmol) portion of 1,1'-bis(3,5-di-*tert*-butyl-2-(2-aminoethoxy)phenyl)ethane was treated with 1.76 g (4.62 mmol) of **7** to afford 2.00 g (90%) of product. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.25 (s, 18 H, CH<sub>3</sub>), 1.33 (s, 18 H, CH<sub>3</sub>), 1.43 (d, 3 H,  $J$  = 8.6 Hz, CHCH<sub>3</sub>), 3.42–3.71 (several multiplets, 8 H, P-CH<sub>2</sub>-C(O) + N-CH<sub>2</sub>CH<sub>2</sub>-O), 3.99 (m, 4 H, N-CH<sub>2</sub>CH<sub>2</sub>-O), 4.70 (q, 1 H,  $J$  = 6.6 Hz, CH), 7.15 (b s, 2 H, Ar-H), 7.18 (b s, 2 H, Ar-H), 7.27–7.47 (m, 12 H, P-Ar), 7.78 (b m, 8 H, P-Ar), 8.27 (b, 3 H, NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 24.07, 31.59, 34.62, 35.51, 38.89, 39.69, 40.26 (aliphatic); 71.94 (O-CH<sub>2</sub>); 122.46, 124.10, 128.69, 128.85, 130.99, 131.12, 132.23, 132.61, 139.40, 141.65, 141.65, 145.36, 153.22 (aromatic); 165.36 (C=O). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  = 30.41. Anal. Calcd for C<sub>62</sub>H<sub>78</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>: C, 73.78; H, 7.79; N, 2.78. Found: C, 73.85; H, 7.98; N, 2.73.

**General Procedure for the Synthesis of 10.** A stirring suspension of triphenoxymethane molecule (**4**),<sup>34</sup> *N*-(3-bromopropyl)-phthalimide and cesium carbonate in DMF was heated to 80–85 °C for 6 days. The reaction mixture was cooled to room temperature and poured into cold water, resulting in formation of a white solid product. The mixture was transferred to a separation funnel and extracted with diethyl ether. The solid product suspended in the ether layer and was collected by filtration and dried.

**Compound 10a.** Using a 10.01 g (14.04 mmol) portion of tris-(3,5-di-*tert*-pentyl-2-hydroxyl)methane (**4a**) afforded 11.53 g (64%) of product. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.50 (m, 18 H; CH<sub>2</sub>CH<sub>3</sub>), 1.13 (s, 18 H; CCH<sub>3</sub>), 1.32 (s, 18 H; CCH<sub>3</sub>), 1.45 (q,  $J$  = 7.4, 6 H; CH<sub>2</sub>CH<sub>3</sub>), 1.70 (q,  $J$  = 7.5, 6 H; CH<sub>2</sub>CH<sub>3</sub>), 2.12 (b, 6 H; CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>), 3.50 (b, 6 H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-N), 4.01 (m, 6 H; O-CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>), 6.42 (s, 1 H; CH), 7.01 (d,  $J$  = 2.3, 3 H; Ar-H), 7.10 (d,  $J$  = 2.1, 3 H; Ar-H), 7.45 (m, 6 H; Ar-H), 7.54 (m, 6 H; Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 9.3, 9.8, 28.8, 29.6, 29.7, 35.1, 36.3, 37.1, 37.9, 39.4 (aliphatic); 69.8 (O-CH<sub>2</sub>); 122.9, 124.9, 128.1, 132.8, 132.9, 133.3, 138.3, 140.1, 142.5, 153.4 (aromatic); 168.3 (C=O). FAB MS  $m/z$  = 1274.77 [M + H]<sup>+</sup>.

**Compound 10b.** The material was obtained in 89% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.19 (s, 27 H; CCH<sub>3</sub>), 1.34 (s, 27 H; CCH<sub>3</sub>), 2.19 (m, 6 H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.58 (t,  $J$  = 5.5, 6 H; CH<sub>2</sub>CH<sub>2</sub>-N), 4.03 (m, 6 H; O-CH<sub>2</sub>CH<sub>2</sub>), 6.48 (s, 1 H; CH), 7.15 (d,  $J$  = 2.3, 2 H; Ar-H), 7.23 (m, 2 H; Ar-H), 7.47 (m, 6 H; Ar-H), 7.54 (m, 6 H; Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 29.6, 31.5, 31.7, 34.7, 35.7, 36.3 (aliphatic); 70.3 (O-CH<sub>2</sub>); 122.4, 122.9, 127.3, 132.8, 133.3,

138.0, 142.2, 144.6, 153.7 (aromatic); 168.3 (C=O). FAB MS  $m/z$  = 1212.66 [M + Na]<sup>+</sup>

**General Procedure for Synthesis of 11a and 11b.** To a suspension of **10** in absolute ethanol, hydrazine mono hydrate (4 equiv) was slowly added and the mixture was refluxed for 24 h. The reaction was cooled to room temperature, and the solvent was partially evaporated under reduced pressure. The resulting residue was poured into ice-cold water and a white precipitate quickly formed. The product was collected by filtration.

**Compound 11a.** Yield 97%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.40–0.49 (m, 18 H, CH<sub>2</sub>CH<sub>3</sub>), 1.04 (s, 18 H, CH<sub>3</sub>), 1.25 (s, 18 H, CH<sub>3</sub>), 1.37 (q,  $J$  = 7.5 Hz, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 1.62 (q,  $J$  = 7.5 Hz, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 1.77 (quintet,  $J$  = 6.6 Hz, 6.9 Hz, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-O), 2.58 (b s, 6 H, NH<sub>2</sub>), 2.80 (t,  $J$  = 6.9 Hz, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>-O), 3.38 (b t, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 6.23 (s, 1 H, CH), 6.95 (s, 6 H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 39.5, 39.4, 39.2, 37.7, 36.9, 35.0, 34.2, 29.5, 28.7, 9.7, 9.2 (aliphatic); 70.4 (O-CH<sub>2</sub>); 153.5, 147.4, 142.3, 139.7, 138.2, 128.0, 124.7 (aromatic). FAB MS  $m/z$  = 884.76 [M + H]<sup>+</sup>.

**Compound 11b.** Yield 92%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.12 (s, 27 H, CH<sub>3</sub>), 1.25 (s, 27 H, CH<sub>3</sub>), 1.83 (quintet,  $J$  = 7.5 Hz, 6.6 Hz, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 2.87 (t,  $J$  = 7.5 Hz, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-O), 3.38 (t,  $J$  = 6.6 Hz, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 6.25 (s, 1 H, CH), 7.10–7.16 (m, 6 H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 31.32, 31.45, 33.17, 34.51, 35.46, 38.50, 38.98 (aliphatic); 70.50 (O-CH<sub>2</sub>); 122.47, 126.0, 127.38, 129.83, 131.79, 137.61, 141.79, 144.68, 153.35 (aromatic). FAB MS  $m/z$  = 800.67 [M + H]<sup>+</sup>.

**General Procedure for the Synthesis of 12a and 12b.** A chloroform solution of 0.75 g of amine (**11**) and 3.1 equiv of *p*-nitrophenyl(diphenylphosphoryl)acetate (**7**) were stirred at 45–50 °C for 3 days. The reaction mixture was cooled to room temperature; 1 M sodium hydroxide solution was added and stirred for 2 h. The organic phase was extracted with 5% sodium carbonate followed by brine, and the solution was dried over MgSO<sub>4</sub>. The solvent was removed in vacuo, and acetonitrile (15 mL) was added resulting in product precipitation. The solid was filtered, washed with acetonitrile, and dried, to afford a pure product.

**Compound 12a.** Yield 70%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.36–0.42 (m, 18 H, CH<sub>2</sub>CH<sub>3</sub>), 1.04 (s, 18 H, CH<sub>3</sub>), 1.15 (s, 18 H, CH<sub>3</sub>), 1.36 (q,  $J$  = 7.5 Hz, 12 H, CH<sub>2</sub>CH<sub>3</sub>), 1.50 (q,  $J$  = 7.5 Hz, 6 H, CH<sub>2</sub>-CH<sub>3</sub>), 1.80 (b s, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 3.23–3.40 (several multiplets, 18 H, P(O)-CH<sub>2</sub>-C(O)N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 6.15 (s, 1 H, CH), 6.88 (d,  $J$  = 1.8 Hz, 3 H, Ar-H), 7.00 (d,  $J$  = 1.8 Hz, 3 H, Ar-H), 7.28–7.48 (m, 18 H, P-Ar H), 7.64–7.84 (m, 12 H, P-Ar H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 9.2, 9.7, 28.7, 29.6, 30.5, 35.1, 37.0, 37.7, 38.1, 39.2, (aliphatic); 69.7 (O-CH<sub>2</sub>); 124.7, 127.9, 128.7, 128.9, 131.1, 131.6, 132.2, 133.0, 137.8, 139.7, 142.3, 147.4, 153.3 (aromatic); 165.22, 165.16 (C=O). <sup>31</sup>P NMR:  $\delta$  = 30.3. ESI FT-ICR MS  $m/z$  = 1633.88 [M + Na]<sup>+</sup>.

**Compound 12b.** Yield 49%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.16 (s, 27 H; CCH<sub>3</sub>), 1.21 (s, 27 H; CCH<sub>3</sub>), 1.91 (b, 6 H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.39 (several multiplets, 18 H; O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-NH-C(O)CH<sub>2</sub>P(O)), 6.28 (s, 1 H; CH), 7.08 (d,  $J$  = 2.3, 3 H; Ar-H), 7.23 (d,  $J$  = 2.6, 3 H; Ar-H), 7.40 (m, 18 H; P-Ar H), 7.77 (m, 12 H; P-Ar H), 7.87 (t,  $J$  = 5.4, 3 H; NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 30.6, 31.6, 31.7, 34.6, 35.6, 38.1, 38.9, 39.7 (aliphatic); 70.3 (O-CH<sub>2</sub>); 122.3, 127.1, 128.7, 128.9, 131.1, 131.2, 131.7, 132.17, 132.21, 133.1, 137.6, 141.9, 144.4, 153.6 (aromatic); 165.2, 165.1 (C=O). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  = 29.8. ESI FT-ICR MS  $m/z$  = 1549.79 [M + Na]<sup>+</sup>.

**Compound 13a.** To a mixture of **6a** (2.16 g, 2.56 mmol) and KOH (4.32 g) in 40 mL of dichloromethane, ethylchloroformate (1.6 mL, 1.82 g, 17 mmol) was added. The mixture was stirred for 3 days at room temperature. The solution was then washed with

200 mL of water and brine (50 mL) and was dried over MgSO<sub>4</sub>. The solvent was evaporated to afford 2.5 g of product in 92% yield. <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ = 0.56 (t, 9 H, CH<sub>2</sub>CH<sub>3</sub>), 0.59 (t, *J* = 7.5, 9 H, CH<sub>2</sub>CH<sub>3</sub>), 1.18 (s, 18 H, CCH<sub>3</sub>), 1.26 (t, *J* = 7.5, 9 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.37 (s, 18 H, CCH<sub>3</sub>), 1.54 (q, *J* = 7.5, 6 H, CH<sub>2</sub>-CH<sub>3</sub>), 1.76 (q, *J* = 7.5, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 3.39–3.65 (b m, 6 H, O-CH<sub>2</sub>CH<sub>2</sub>-N + 6 H, O-CH<sub>2</sub>CH<sub>2</sub>-N), 4.12 (q, *J* = 7.2, 6 H, O-CH<sub>2</sub>CH<sub>3</sub>), 6.42 (s, 1 H, CH), 7.15 (b, 6 H, Ar-H). <sup>13</sup>C NMR (CD<sub>3</sub>OD): δ = 9.8, 10.2, 15.2, 29.3, 30.3, 36.3, 38.0, 38.9, 40.4, 42.4 (aliphatic); 62.0 (CH<sub>2</sub>-O); 72.0 (CH<sub>2</sub>-OAr); 126.4, 129.1, 139.3, 141.4, 144.2, 154.4 (aromatic); 159.1 (C=O). LSI MS: *m/z* = 1058.77 [M + H]. Anal. Calcd for C<sub>64</sub>H<sub>103</sub>N<sub>3</sub>O<sub>9</sub>: C, 72.62; H, 9.81; N, 3.97; Found: C, 72.86; H, 10.30; N, 3.90.

**Compound 13b.** To a mixture of amine **11b** (5 g, 6.3 mmol) and KOH (11.4 g) in 20 mL of dichloromethane, ethylchloroformate (2.8 mL, 3.2 g, 29 mmol) was added. The mixture was stirred for 3 days at room temperature. Subsequently, the solution was washed with 250 mL of water and brine (50 mL), dried over MgSO<sub>4</sub>, and evaporated. Yield: 75% (4.75 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.18 (s, 27 H, CH<sub>3</sub>), 1.23 (t, *J* = 6.90 Hz, 9 H, CH<sub>3</sub>), 1.33 (s, 27 H, CH<sub>3</sub>), 1.98 (m, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 3.39 (m, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-O), 3.52 (m, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 4.11 (q, *J* = 6.20 Hz, 6 H, O-CH<sub>2</sub>CH<sub>3</sub>), 5.39 (b s, 3 H, NH), 6.35 (s, 1 H, CH), 7.13–7.26 (m, 6 H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.9, 30.9, 31.6, 34.6, 35.7, 39.1, 60.7, 71.0 (aliphatic); 122.6, 127.3, 144.7, 137.8, 141.9, 153.6 (aromatic); 157.1 (C=O). FAB MS: *m/z* = 1016.73 [M + H]<sup>+</sup>. Anal. Calcd for C<sub>61</sub>H<sub>97</sub>N<sub>3</sub>O<sub>9</sub>: C, 72.08; H, 9.62; N, 4.13; Found: C, 72.07; H, 9.88; N, 4.06.

**Compound 14a.** To a stirred solution of lithium aluminum hydride (2.53 g, 0.067 mol) in tetrahydrofuran (500 mL) at 0 °C, 2.4 g (2.27 mmol) of ester **13a** was added dropwise, and the reaction mixture was stirred at room temperature for 5 days. To quench LAH, the solution was cooled to 0 °C, treated with 3 mL of water and stirred for 5 min. A total of 3 mL of 15% NaOH was then added dropwise, and after an additional 30 min, more water (9 mL) was added (Steinhard's method).<sup>35</sup> The solid was separated, and the organic phase was dried over MgSO<sub>4</sub>. The solution was evaporated to give crude product that was further purified by precipitation in acidified pentane, dissolution in diethyl ether, and extraction with 1M NaOH. The organic phase was dried with MgSO<sub>4</sub> and evaporated to yield 2 g (95%) of pure product. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.55 (t, *J* = 7.2 Hz, 9 H, CH<sub>2</sub>CH<sub>3</sub>), 0.57 (t, *J* = 7.2 Hz, 9 H, CH<sub>2</sub>CH<sub>3</sub>), 1.13 (s, 18 H, CH<sub>3</sub>), 1.35 (s, 18 H, CH<sub>3</sub>), 1.47 (q, *J* = 7.5 Hz, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 1.73 (q, *J* = 7.5 Hz, 6 H, CH<sub>2</sub>-CH<sub>3</sub>), 2.47 (s, 9 H, NCH<sub>3</sub>), 2.43 (b t, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>-O), 3.65 (t, *J* = 5.7 Hz, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>-O), 6.36 (s, 1 H, CH), 6.99 (b, 3 H, Ar-H), 7.05 (b, 3 H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 9.3, 9.7, 28.8, 29.7, 35.35, 36.9, 37.1, 37.8, 39.3 (aliphatic); 52.2 (N-CH<sub>2</sub>); 71.7 (O-CH<sub>2</sub>); 124.9, 127.9, 138.0, 139.8, 142.6, 153.4 (aromatic). LSI MS: *m/z* = 884.76 [M + H]<sup>+</sup>.

**Compound 14b.** To a stirring solution of ester **13b** (7.0 g, 0.0069 mol) in tetrahydrofuran (500 mL) in ice-cold conditions, lithium aluminum hydride (2.8 g, 0.074 mol) was slowly added. The reaction mixture was stirred at room temperature for 6 days. The reaction mixture was cooled to ice-cold temperature, 1M NaOH (50 mL) was added, and the stirring was continued for 15 min. Then, water (100 mL) was added and the content was transferred to separating funnel and extracted with diethyl ether (4 × 50 mL). The organic phase was washed with brine (5 × 20 mL), dried over MgSO<sub>4</sub>, and evaporated to give 5.04 g (87%) of pure product. <sup>1</sup>H

NMR (CDCl<sub>3</sub>): δ = 1.18 (s, CH<sub>3</sub>, 27 H), 1.34 (s, CH<sub>3</sub>, 27 H), 1.95 (t, *J* = 7.35 Hz, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 2.43 (s, 9 H, CH<sub>3</sub>), 2.73 (t, *J* = 7.35 Hz, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 3.54 (t, *J* = 6.30 Hz, 6 H, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 6.36 (s, 1 H, CH), 7.12–7.26 (m, 6 H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 30.8, 31.6, 31.7, 34.6, 35.6, 36.6, 38.8 (aliphatic); 49.3 (N-CH<sub>3</sub>); 71.0 (O-CH<sub>2</sub>); 122.6, 127.3, 138.0, 141.8, 144.3, 147.4, 153.9 (aromatic). FAB MS: *m/z* = 842.71 [M + H]<sup>+</sup>.

**Compound 15a.** To a solution of the secondary amine **14a** (2.42 g, 2.74 mmol) and K<sub>2</sub>CO<sub>3</sub> (4.50 g, 32.56 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added chloroacetyl chloride (1.40 mL, 17.60 mmol), and the reaction mixture was refluxed for 18 h. A second portion of chloroacetyl chloride (0.70 mL, 8.80 mmol) was added and refluxed for an additional 20 h. Subsequently, the solution was cooled down, washed with 2 N NaOH and H<sub>2</sub>O, and dried over MgSO<sub>4</sub>. The solvent was removed in vacuo, and the crude white solid was recrystallized from dichloromethane/hexamethyl-disiloxane to give 2.70 (88%) g of pure product. <sup>1</sup>H NMR (CDCl<sub>3</sub>) as well as <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectra are very complicated. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.51–0.60 (m, 18 H, CH<sub>2</sub>CH<sub>3</sub>), 1.12 (b, 18 H, CH<sub>3</sub>), 1.30 (b, 18 H, CH<sub>3</sub>), 1.44–1.73 (b m, 12 H, CH<sub>2</sub>CH<sub>3</sub>), 2.88–4.22 (several multiplets, 9 HN-CH<sub>3</sub> + 6 HN-CH<sub>2</sub>CH<sub>2</sub>-O + 6 H, N-CH<sub>2</sub>CH<sub>2</sub>-O), 4.06 (s, 6 H, CH<sub>2</sub>-Cl), 6.33, 6.38, 6.43 (s, 1 H, CH), 6.82–7.11 (m, 6 H, Ar-H). LSI MS: *m/z* = 1112.67 [M + H]<sup>+</sup>.

**Compound 15b.** To a solution of the secondary amine **14b** (3.00 g, 3.60 mmol) and K<sub>2</sub>CO<sub>3</sub> (6.00 g, 43.40 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added chloroacetyl chloride (2.08 mL, 26.15 mmol), and the reaction mixture was heated at 45 °C for 12 h. A second portion of chloroacetyl chloride (1.04 mL, 13.07 mmol) was added and stirred for an additional 20 h at 45 °C. Subsequently, the solution was cooled down washed with 2 N NaOH and H<sub>2</sub>O, and dried over MgSO<sub>4</sub>. The solvent was removed in vacuo to give 2.50 g (66%) of pure product. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.18 (s, 27 H, CH<sub>3</sub>), 1.36 (s, 27 H, CH<sub>3</sub>), 1.84–1.95 (m, 6 H O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-N), 2.86–3.04 (m, 9 H, N-CH<sub>3</sub>), 3.37–3.65 (b m, 6 H, O-CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>-N + 6 H, CH<sub>2</sub>-Cl), 4.04–4.10 (m, 6 H, O-CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-N), 6.33 (s, 1 H, CH), 7.20–7.11 (m, 6 H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 27.9, 29.3, 31.6, 33.7, 34.6, 35.7, 39.1, 41.1, 41.8, 46.347.9 (aliphatic); 70.4 (OCH<sub>2</sub>); 122.6, 127.5, 137.9, 141.8, 144.9, 153.5 (aromatic) 166.2 (C=O). EI MS *m/z* = 1071.61 [M + H]<sup>+</sup>. Anal. Calcd for C<sub>61</sub>H<sub>94</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>6</sub>: C, 68.36; H, 8.84; N, 3.92; Found: C, 68.58; H, 8.31; N, 3.71.

**Compound 16a. Method A.** The 2.50 g, 2.24 mmol of starting material (**15a**) was dissolved in 9.00 mL of ethyl diphenylphosphinite (9.59 g, 41.65 mmol) while the temperature was gradually increased from 100 to 150 °C and the mixture was stirred for 40 h. Subsequently, the reaction mixture was cooled down to room temperature, and the diisopropyl ether was added until a white precipitate was formed. The solid was filtered and washed with diisopropyl ether to afford 3.08 g (85%) of pure product. <sup>1</sup>H NMR (CDCl<sub>3</sub>) as well as <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectra are very complicated. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.44–0.53 (m, 18 H, CH<sub>2</sub>CH<sub>3</sub>), 1.04 (s, 9 H, CH<sub>3</sub>), 1.09 (s, 9 H, CH<sub>3</sub>), (these two singlets merge into one δ = 1.8 at 55 °C), 1.21 (s, 9 H, CH<sub>3</sub>), 1.27 (s, 9 H, CH<sub>3</sub>), (these two singlets merge into one δ = 1.25 at 55 °C), 1.42 (b m, 6 H, CH<sub>3</sub>), 1.62 (b m, 6 H, CH<sub>3</sub>), 2.66–3.69 (several multiplets, 9 H, N-CH<sub>3</sub> + 6 H N-CH<sub>2</sub>CH<sub>2</sub>-O + 6 H, N-CH<sub>2</sub>CH<sub>2</sub>-O), 6.21, 6.26, 6.32 (s, 1 H, CH), 6.83–7.02 (m, 6 H, Ar-H), 7.44–7.53 (m, 18 H, P-Ar H), 7.84–7.90 (m, 18 H, P-Ar H). ESI FT-ICR MS *m/z* = 827.94 [M + 2Na]<sup>2+</sup>, *m/z* = 1632.89 [M + Na]<sup>+</sup>. Anal. Calcd for C<sub>100</sub>H<sub>130</sub>N<sub>3</sub>O<sub>9</sub>P<sub>3</sub>: C, 74.55; H, 8.13; N, 2.61; Found: C, 74.34; H, 8.44; N, 2.61. Slow diffusion of pentane into a solution of **16a** in diethyl ether/dichloromethane afforded crystals suitable

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for X-ray analysis. **Method B.** A solution of secondary amine (0.47 g, 0.53 mmol) and *p*-nitrophenyl (diphenylphosphoryl)acetate (1.10 g, 2.88 mmol) in dichloromethane was stirred for 2 weeks at room temperature. Subsequently, the solution was treated with 1 M NaOH and stirred for additional 2 h. The *p*-nitrophenol salt was extracted from the organic phase using 5% sodium carbonate. The organic phase was dried over MgSO<sub>4</sub>, filtered, and the solvent was removed in vacuo. The crude product was criticized by the diffusion of pentane into a solution of the product in diethyl ether/dichloromethane; yield 0.60 g (70%).

**Compound 16b. Method A.** The 0.50 g, 0.47 mmol of starting material (**15b**) was suspended in 1.00 mL of ethyl diphenylphosphinite (4.20 mmol) while the temperature was gradually increased from 100 to 150 °C. Within first 3 h of the reaction, every 20 min the mixture was exposed for few seconds to the vacuum. The reaction mixture was stirred at 150 °C for an additional 20 h. Subsequently, it was cooled down to room temperature, and the diethyl ether was added until a white precipitate was formed. The solid was filtered and redissolved in diisopropyl ether to give a pure product upon crystallization. Yield 0.42 g (57%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) as well as <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectra are very complicated. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.15 (s, 27 H, CH<sub>3</sub>), 1.27 (s, 27 H, CH<sub>3</sub>), 1.78–1.95 (m, 6 H, N–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–O), 2.66–3.55 (several multiplets, 27 H: 9 H N–CH<sub>3</sub> + 6 H N–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–O + 6H, N–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–O), 6.24 (b s, 1 H, CH), 6.93 (b s, 2 H, Ar–H), 7.06 (b s, 2 H, Ar–H), 7.38 (m, 18 H, P–Ar H), 7.74 (m, 12 H, P–Ar H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 27.9, 29.4, 31.5, 33.9, 34.5, 35.5, 36.9, 37.7, 38.6, 38.9, 46.0, 48.3 (aliphatic); 70.6 (O–CH<sub>2</sub>); 122.3, 127.2, 128.6, 128.7, 131.2, 131.3, 132.1, 133.3, 137.7, 141.7, 144.5, 144.7, 153.5 (aromatic); 164.8 (C=O). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ = 29.4, 29.3. EI MS *m/z* = 1567.86 [M + H]<sup>+</sup>. **Method B.** A solution of secondary amine (2.00 g, 2.40 mmol), *p*-nitrophenyl (diphenylphosphoryl)acetate (4.50 g, 11.80 mmol), and 1 mL of Et<sub>3</sub>N in chloroform, was stirred for 5 days at 45–50 °C. After cooling down to room temperature, the solution was treated with 1 M NaOH and stirred for an additional 2 h. The *p*-nitrophenol salt was extracted from the organic phase using 5% sodium carbonate. The organic phase was dried over MgSO<sub>4</sub>, filtered, and the solvent was removed in vacuo. The crude product was washed with diethyl ether and dried, yielding 2.50 g (67%) of clean product.

**Terbium Complex of 8a [8a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>.** To a solution of **8a** (0.200 g, 0.127 mmol) in acetonitrile (8 mL), Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.058 g, 0.128 mmol) in methylene chloride (4.5 mL) was added, and the reaction mixture was stirred overnight at room-temperature, resulting in a white solid. The complex was isolated by filtration, washed with acetonitrile, and dried. Yield 0.180 g (74%). Anal. Calcd for C<sub>97</sub>H<sub>124</sub>N<sub>6</sub>O<sub>18</sub>P<sub>3</sub>Tb: C, 60.87; H, 6.53; N, 4.39. Found: C, 60.91; H, 6.66; N, 4.27. Slow diffusion of ether into a concentrated solution of the complex in methanol afforded crystals suitable for structural analysis.

**Terbium Complex of 16a [16a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>.** A solution of Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.028 g, 0.062 mmol) in 1 mL of methanol was added to a solution of **16a** (0.100 g, 0.062 mmol) in methanol (1 mL), and reaction mixture was stirred for 1 h at room temperature. A white precipitate formed within minutes, and the product was collected by filtration, washed with cold methanol, and dried to obtain 0.080 g (62%) of product. ESI FT–ICR MS *m/z* = 915.40 [16a·TbNO<sub>3</sub>]<sup>2+</sup>. Slow diffusion of ether into a concentrated solution of the complex in a mixture of methanol and dichloromethane afforded crystals suitable for structural analysis.

**Bismuth Complex of 8c [8c·BiNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>.** A solution of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.058 g, 0.12 mmol) in 8 mL of a 1:1 mixture of acetonitrile and methanol was added to a solution of **8c** (0.08 g,

0.06mmol) in 2 mL of methanol, and the mixture was stirred for 1 h. Part of the solvent was evaporated in vacuo, and the product was precipitated out by ether diffusion. Yield 0.080 g (52%). Slow diffusion of ether into a saturated acetonitrile/methanol solution of [8c·Bi(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub> afforded crystals suitable for structural analysis. <sup>1</sup>H NMR (CD<sub>3</sub>CD<sub>2</sub>, 55 °C): δ = 1.15 (s, 27 H; Ar–C(CH<sub>3</sub>)<sub>3</sub>), 2.14 (s, 9 H; Ar–CH<sub>3</sub>), 3.17 (b, 12H; 3.96 Ar–O–CH<sub>2</sub>CH<sub>2</sub>), 6.74 (s, 1 H; C–H), 7.00 (d, *J* = 2.05 Hz, 3 H; Ar *H*), 7.10 (d, *J* = 2.56 Hz, 3 H; Ar *H*), 7.49 (m, 12 H; P–Ar *H*), 7.62 (m, 6H; P–Ar *H*), 7.74 (m, 12 H; P–Ar *H*), 7.86 (s, 3 H; N–H). <sup>31</sup>P NMR (CDCl<sub>3</sub>): = 39.66. HR ESI–ICR MS (sample injected as solution in 1% HNO<sub>3</sub>/MeOH): *m/z* = 814.29 [8c·Bi(NO<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> and *m/z* = 1691.56 [8c·Bi(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>83</sub>H<sub>102</sub>BiN<sub>6</sub>O<sub>21</sub>P<sub>3</sub>: C 54.73; H 5.64; N 4.61; Found: C, 54.54; H, 5.32; N, 4.92.

**X-ray Crystallography.** Unit cell dimensions and intensity data for all of the structures were obtained on a Siemens CCD SMART diffractometer at 173 K. The data collections nominally covered a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal, and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.0 cm. The data sets were corrected empirically for absorption using SADABS.

All of the structures were solved using the Bruker SHELXTL software package for the PC, using either the direct methods or Patterson functions in SHELXS. The space groups of the compounds were determined from an examination of the systematic absences in the data, and the successful solution and refinement of the structures confirmed these assignments. All of the hydrogen atoms were assigned idealized locations and were given a thermal parameter equivalent to 1.2 or 1.5 times the thermal parameter of the atom to which it was attached. For the methyl groups, where the location of the hydrogen atoms is uncertain, the AFIX 137 card was used to allow the hydrogen atoms to rotate to the maximum area of residual density, while fixing their geometry. In cases of extreme disorder or other problems, the non-hydrogen atoms were refined isotropically, and hydrogen atoms were not included in the model. Severely disordered solvents were removed from the data for **12a**, **16a**, [8a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>, [8c·BiNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> using the SQUEEZE function in the *Platon for Windows* software, and the details are reported in the Supporting Information in the CIF file for each structure. Structural and refinement data and selected bond lengths for all of the compounds are presented in the Table 1.

## Results and Discussion

**Synthesis of Tris-CMPO Ligands with Two-Carbon Linkers to Platform.** A 3:1 CMPO-to-metal stoichiometry has been suggested for americium species extracted from the acidic aqueous phase into the organic phase during the TRUEX process,<sup>36–38</sup> and to facilitate the extraction, we envisioned that a single ligand with three CMPO arms extended out from a molecular platform could greatly enhance the binding and extraction of the metal ions from an acidic solution. In our previous work with the triphenoxymethane ligand, this base favored a conformation with the three phenolic oxygen atoms orientating themselves “all up” (Figure 2), relative to the central

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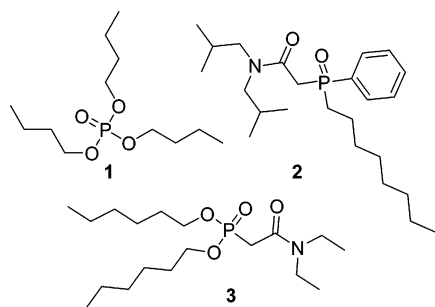
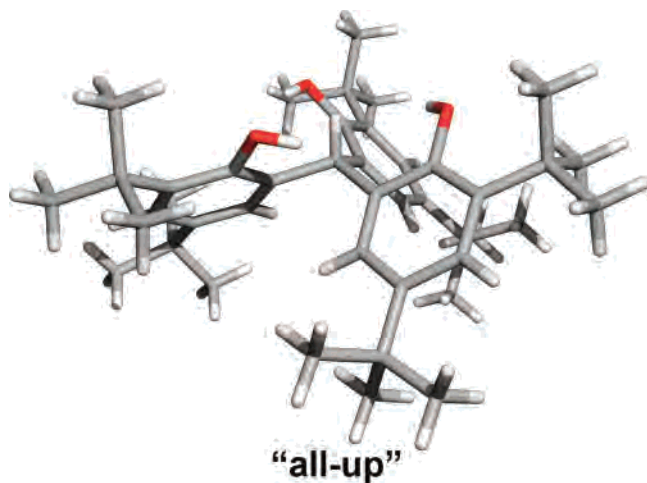
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**Table 1.** X-ray Data<sup>a</sup> for the Crystal Structures of **12b**, **16a**, and the Complexes [**8a**·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>, [**16a**·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>, and [**8c**·BiNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>

	<b>12b</b> ·CH <sub>3</sub> OH	<b>16a</b> ·3CHCl <sub>3</sub> ·1/2Et <sub>2</sub> O	[ <b>8a</b> ·TbNO <sub>3</sub> ] (NO <sub>3</sub> ) <sub>2</sub> Et <sub>2</sub> O	[ <b>16a</b> ·TbNO <sub>3</sub> ] (NO <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub> OH	[ <b>8c</b> ·BiNO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>
total reflns	24 103	32 269	31 069	23 269	51 156
unique reflns	5195	20 440	19 665	14 248	30 858
Θ <sub>max</sub> (deg)	24.99	25.00	25.00	23.00	24.50
empirical formula	C <sub>95</sub> H <sub>122</sub> N <sub>3</sub> O <sub>10</sub> P <sub>3</sub>	C <sub>105</sub> H <sub>138</sub> Cl <sub>9</sub> N <sub>3</sub> O <sub>9.5</sub> P <sub>3</sub>	C <sub>101</sub> H <sub>134</sub> N <sub>6</sub> O <sub>19</sub> P <sub>3</sub> Tb	C <sub>101</sub> H <sub>134</sub> N <sub>6</sub> O <sub>19</sub> P <sub>3</sub> Tb	C <sub>82</sub> H <sub>94</sub> BiN <sub>6</sub> O <sub>18</sub> P <sub>3</sub>
M <sub>r</sub>	1558.87	2006.14	1987.97	1987.97	1753.52
cryst syst	hexagonal	triclinic	triclinic	triclinic	triclinic
space group	R3	P1	P1	P1	P1
a (Å)	18.674(2)	17.250(2)	12.5597(9)	12.4105(18)	20.8891(13)
b (Å)		18.070(2)	15.5209(12)	13.713(2)	22.9583(15)
c (Å)	43.801(3)	21.557(3)	28.949(2)	33.122(5)	23.1141(15)
α (deg)		87.288(2)	93.700(2)	88.353(3)	80.308(1)
β (deg)		66.965(2)	90.632(2)	82.941(2)	64.914(1)
γ (deg)		71.870(2)	90.532(2)	66.989(2)	68.352(1)
V <sub>c</sub> (Å <sup>3</sup> )	13228(2)	5855.5(13)	5630.9(7)	5148.0(13)	9330.4(10)
D <sub>calcd</sub> (g cm <sup>-3</sup> )	1.174	1.138	1.172	1.282	1.294
T (K)	173(2)	173(2)	173(2)	173(2)	193(2)
Z	6	2	2	2	4
μ(Mo Kα) (mm <sup>-1</sup> )	0.126	0.307	0.732	0.801	2.004
R1 [I ≥ 2σ(I) data] <sup>b</sup>	0.0816 [3938]	0.0826 [13367]	0.0682 [11826]	0.0970 [11988]	0.0657 [15711]
wR2 (all data) <sup>c</sup>	0.1980	0.2673	0.1610	0.2090	0.1780
GOF	1.140	1.115	0.901	1.274	0.899

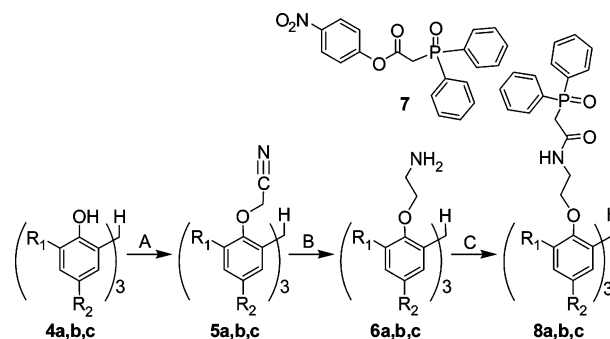
<sup>a</sup> Obtained with monochromatic Mo Kα radiation (λ = 0.71073 Å). <sup>b</sup> R1 = Σ||F<sub>o</sub>| - |F<sub>c</sub>||/Σ|F<sub>o</sub>|. <sup>c</sup> wR2 = {Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)/Σ[w(F<sub>o</sub><sup>2</sup>)]}<sup>1/2</sup>.

**Figure 1.** Common organophosphorus extractants **1**-TBP, **2**-CMPO, and **3**-DHDECMP.**Figure 2.** Depiction of the “all up” conformation of the phenolic oxygens on the triphenoxymethane platform with respect to its central methane hydrogen generated from crystallographic coordinates.

methine hydrogen both in the solid-state and in solution.<sup>28,34,39,40</sup> Tethering three CMPO moieties to this platform via these phenol oxygens satisfies the requirement for

(39) Matloka, K.; Gelis, A.; Regalbuto, M.; Vandegrift, G.; Scott, M. J. *J. Chem. Soc., Dalton Trans.* **2005**, 3719–3721.

(40) Matloka, K.; Gelis, A.; Regalbuto, M.; Vandegrift, G. F.; Scott, M. J. *Sep. Sci. Technol.* **2006**, *41*, 2129.

**Scheme 1**<sup>a</sup>

a: R<sub>1</sub>, R<sub>2</sub> = *t*-Pentyl  
b: R<sub>1</sub>, R<sub>2</sub> = *t*-Bu  
c: R<sub>1</sub> = Me, R<sub>2</sub> = *t*-Bu

<sup>a</sup> Key: (A) NaI, K<sub>2</sub>CO<sub>3</sub>, chloroacetonitrile, refluxing acetone, 3 days; (B) LAH, diethyl ether; (C) *p*-nitrophenyl(diphenylphosphoryl)acetate (**7**), 45–50 °C chloroform.

proximate metal-binding CMPO groups. With the triphenoxymethane platform, the alkyl group on the ortho position of the phenol moderates the solubility of the platform in organic solvents as well as exerts an influence on the extended arms. Large, bulky groups such as *tert*-pentyl increase the solubility but also restrict the flexibility of the three arms tethered to the phenolic arms. To compare the properties of different variants of our ligand system, two new tris-CMPO derivatives were synthesized (**8a** and **8c**). The CMPO moieties were tethered to the altered platform using well-established methodology developed for the CMPO-calix[4]arene systems as outlined for the **8a–c** in Scheme 1.<sup>19,32</sup>

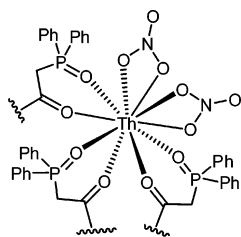
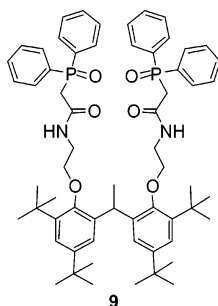
**Extraction and Binding Properties of Tris-CMPO Ligands, 8, with Two-Carbon Linker Arms.** The results have shown a significant solubility variation within the studied *t*-pentyl, *t*-Bu, and Me derivatives (**8a**, **b**, and **c**). All three compounds are readily soluble in most common organic solvents such as dichloromethane, THF, or methanol, but in less polar solvents, the solubility of the methyl



**Table 2.** Percent of Metal Extracted (%E)<sup>a,b</sup> from 1 M Nitric Acid Solution by Ligands: **8a**, **8b**, and **8c**; Aqueous Phase: 10<sup>-4</sup> Metal Nitrate in 1 M HNO<sub>3</sub>, Organic Phase: 10<sup>-3</sup> M Ligand in Methylene Chloride

ligand	<b>8a</b>	<b>8b</b>	<b>8c</b>
cation	%E	%E	%E
Th(IV)	100	98	99
La(III)	3	4	10
Ce(III)	1	5	9
Nd(III)	4	3	8
Eu(III)	2	3	4
Yb(III)	4	10	6

<sup>a</sup> E% = 100% ([M<sup>n+</sup>]<sub>org</sub>/[M<sup>n+</sup>]<sub>total</sub>) after extraction as determined by an Arsenazo(III) assay. <sup>b</sup> Mean value of at least four measurements. The precision:  $\sigma_{(n-1)} = \pm 1$ , where  $\sigma_{(n-1)}$  is a standard deviation from the mean value.

**Figure 3.** Diagrams of the 10-coordinate +2 cationic thorium(IV) nitrate complex of **8b** with 2-coordinated NO<sub>3</sub><sup>-</sup> counterions. Complete structure is presented in ref 28.**Figure 4.** Bis-CMPO ligand (**9**).

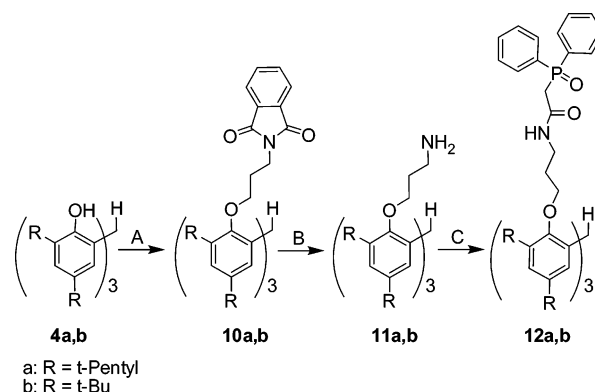
derivative (**8c**) is significantly limited. Of the three, only the *t*-pentyl derivative, **8a**, is compatible with 1-octanol. Despite the solubility differences and steric variations in the platforms, the modifications at the 2 position of the phenols do not significantly affect the affinity of the tris-CMPO ligands for Th(IV), as presented in Table 2. There does appear, however, to be a small increase in affinity for the lighter lanthanides as the size of these groups at the 2 position decreases, and **8c** exhibits a slightly higher affinity for La(III) in comparison to **8a** and **8b**.

The crystal structures of thorium and trivalent metal nitrates of **8b**<sup>28</sup> and **8c** showed three CMPO arms tightly bound to the metal center, which allowed space on the metals for only one (in the case of Ln(III)) and two (in the case of Th(IV), Figure 3) nitrate ions, generating dicationic complexes. In view of the fact that <sup>31</sup>P NMR and FT-ICR-MS have confirmed the existence of these species in solution, the affinity of the organic phase for these charged complexes might be limited. Therefore, the bis-CMPO ligand (**9**) was synthesized using procedures similar to those used in Scheme 1.

**Table 3.** Percent of Metal Extracted (%E)<sup>a,b</sup> from 1 M Nitric Acid Solution by Bis-CMPO Ligand **9** and Mono-CMPO, **2**; Aqueous Phase: 10<sup>-4</sup> M Metal Nitrate in 1 M HNO<sub>3</sub>, Organic Phase: 3 × 10<sup>-3</sup> M of **2**<sup>c</sup>, and 10<sup>-3</sup> M of **9** in Methylene Chloride

ligand	<b>9</b>	<b>2</b>
cation	%E	%E
Th(IV)	4	2
La(III)	10	5
Ce(III)	6	6
Nd(III)	6	6
Eu(III)	6	7
Yb(III)	3	8

<sup>a</sup> E% = 100% ([M<sup>n+</sup>]<sub>org</sub>/[M<sup>n+</sup>]<sub>total</sub>) after extraction as determined by an Arsenazo(III) assay. <sup>b</sup> Mean value of at least four measurements. The precision:  $\sigma_{(n-1)} = \pm 1$ , where  $\sigma_{(n-1)}$  is a standard deviation from the mean value. <sup>c</sup> Three-times higher concentration of classical CMPO was used to keep the same concentration of ligating units in the organic phase.

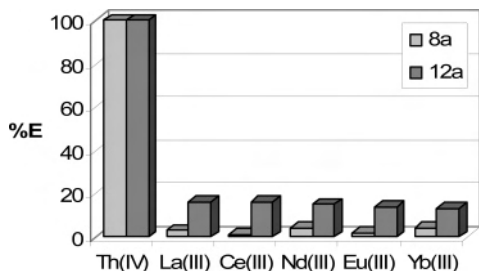
**Scheme 2**<sup>a</sup>

<sup>a</sup> Key: (A) N-(3-bromopropyl)phthalimide, Cs<sub>2</sub>CO<sub>3</sub>, 80–85 °C DMF, 6 days; (B) hydrazine mono hydrate, refluxing ethanol, 24h; (C) *p*-nitrophenyl(diphenylphosphoryl)acetate (**7**), 45–50 °C chloroform, 3 days.

With only two CMPO arms available for the metal, we envisioned that there should be more space in the coordination sphere of the metal for the binding of an additional one or two nitrate counterions. With the resulting reduction in positive charge of the complex, the material would have enhanced solubility in the organic phase. The extraction results revealed, however, that the change from three to two arms severely diminished the effectiveness of **9** for the extraction. In fact, the bis-CMPO ligand showed very similar extraction behavior to the simple CMPO extractant (**2**) (Table 3). Ligand **9** had very low affinity for Th(IV) as well as the series of lanthanides. Apparently, three preorganized CMPO arms are essential to fulfill the geometry requirements around the metal center and afford an appreciable extraction percentage.

**Synthesis of Tris-CMPO Ligands with Three-Carbon Arms.** Extensive work on CMPO-like molecules utilizing calix[4]arene as a platform has found that there is a significant influence of ligand flexibility on its extraction performance.<sup>21</sup> Calix[4]arene extractants showed a strong increase of the extraction percentage with increased length of the spacer between the amido and phenoxy group. Thus, as proposed by the authors,<sup>21</sup> one can anticipate a direct correlation between the size of the cavity and the flexibility of the ligand and its affinity for a particular cation. The increased flexibility of the molecule should indeed allow for better accommodation of metal ions because of the ability

**Chart 1.** Percent of Metal Extracted (%E) from 1 M Nitric Acid Solution by Tris-CMPO Ligands with a Two-Carbon Linker to Platform, **8a**, and a Longer Three-Carbon Linker, **12a**, Using  $10^{-4}$  M Metal Nitrate in 1 M Nitric Acid and  $10^{-3}$  M Ligand in Methylene Chloride

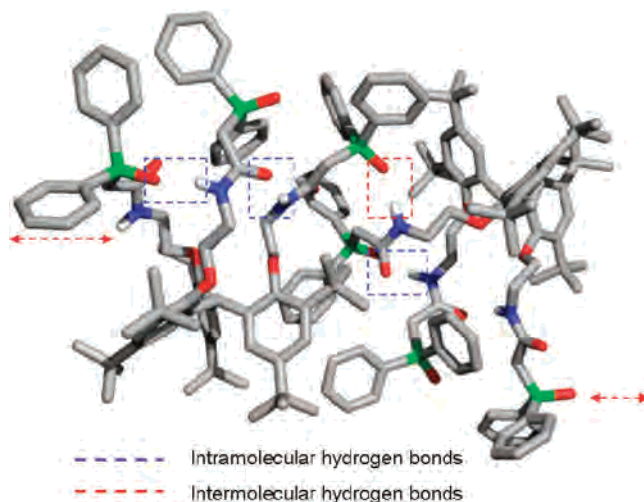


of the molecule to form a more appropriate cavity size. To exercise this postulate, derivatives of the tris-CMPO system with an extended arm length between the platform and the CMPO donors were synthesized. Methodology to isolate a primary amine with a three-carbon spacer to the phenolic oxygen of the triphenoxymethane was adapted from the preparation of calix[4]arene-based extractants (Scheme 2).<sup>21</sup>

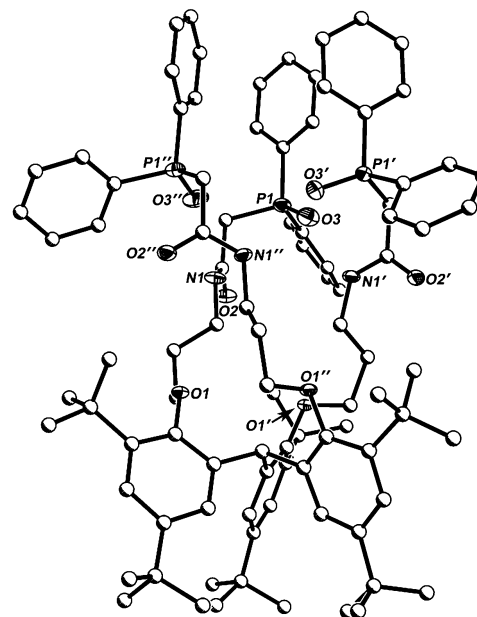
Products **12a** and **12b** were obtained via alkylation of the triphenoxymethane platform with *N*-(3-bromopropyl)phthalimide in the presence of cesium carbonate. The subsequent treatment with hydrazine in ethanol to remove the phthalimide afforded 97% of primary amine **11a** and 92% of **11b**, respectively. Final products were obtained in 70% for **12a** and 49% for **12b** yields.

**Comparison of the Extraction Efficiency of Tris-CMPO Ligands with Two- and Three-Carbon Arms.** The results of the extraction experiment revealed an anticipated increase in the affinity of ligand **12a** over more-rigid **8a** for the studied metal ions, although without any expected significant decrease in Th(IV) selectivity (Chart 1). The increase in the length of the arm, however, did result in a small increase in the binding effectiveness for the lanthanides, presumably due to the increased flexibility of the binding groups.

**Solution Properties and Solid-State Structures of Tris-CMPO Ligands with Two- and Three-carbon Linkers, 8 and 12.** The choice of solvents represents one of the most important factors in liquid–liquid separation science. To achieve effective phase separation, nonpolar solvents should be used. Because of safety concerns, the high boiling and flash points and the low toxicity of the solvent are as equally important as the polarity for waste cleanup operations. Therefore, to find an application in nuclear waste decontamination, compatibility of the tris-CMPO ligand system with aliphatic solvents would be highly desirable, and this trait can be achieved either by altering the structure of the ligand itself or by the addition of a synergist. The solubility studies of **8b** confirmed that the addition of TBP as a synergist indeed induces a defined increase in the solubility of the extractant. Unfortunately, the effect is only temporary, and the tris-CMPO ligand eventually precipitates from the solution. This phenomenon can most likely be attributed to the formation of both intra- and intermolecular hydrogen bonds. In the previously published<sup>28</sup> solid-state structure of **8b** there are two strong hydrogen bonds present between the amide hydrogens and the phosphoryl and carbonyl oxygens on adjacent arms ( $\text{P}=\text{O}\cdots\text{N}_{\text{amide}}$ , 2.801 Å;  $\text{C}=\text{O}\cdots\text{N}_{\text{amide}}$ ,



**Figure 5.** Fragment of the crystal structure of **8b** molecules forming a hydrogen bond connected network. (Crystals obtained by slow diffusion of pentane into a saturated solution of **8b** in methylene chloride).

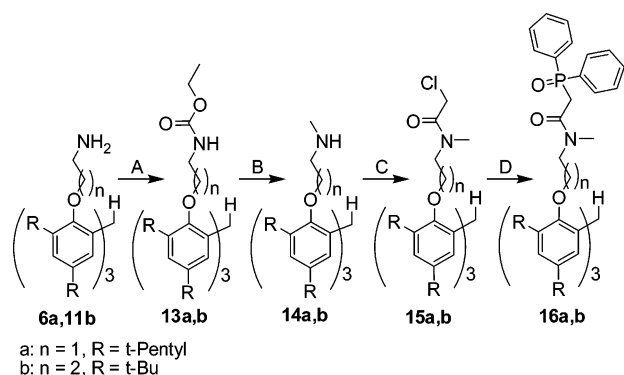


**Figure 6.** Diagram of the solid-state structure of **12b** (30% probability ellipsoids for nitrogen, oxygen, and phosphorus atoms; carbon atoms drawn with arbitrary radii). For clarity, all of the hydrogen atoms have been omitted.

2.798 Å) as well as the intermolecular hydrogen bonds between the phosphoryl oxygens on one ligand and the remaining amide hydrogens on another (Figure 5).

The crystal structure of **12b** presented in Figure 6 significantly differs from the more-rigid **8b**. In place of the extended hydrogen bond network, all three arms form only intramolecular hydrogen bonds between phosphoryl oxygens and adjacent amide hydrogens ( $\text{P}=\text{O}\cdots\text{N}$ , 2.809 Å), constructing a rigorously  $\text{C}_3$ -symmetric structure in the solid state. The aliphatic solvent may force these aromatic molecules to aggregate, further decreasing their solubility, resulting in precipitation.

**Alkylation of Amide Nitrogen for Increased Solubility.** To prevent formation of the problematic hydrogen bonds,

Scheme 3<sup>a</sup>

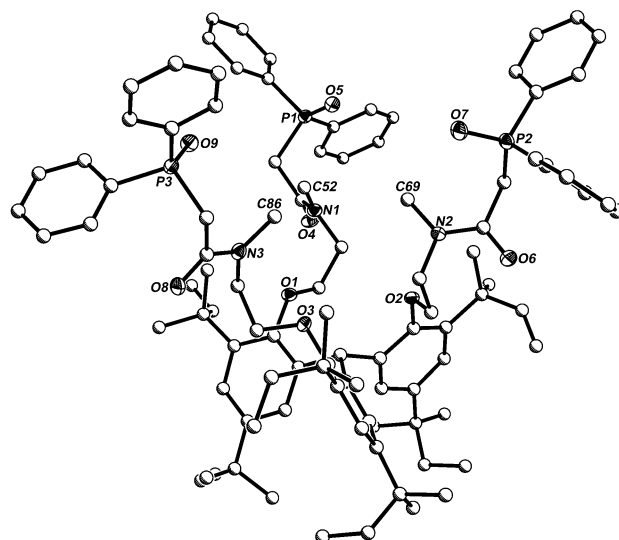
<sup>a</sup> Key: (A) ethylchloroformate, K<sub>2</sub>CO<sub>3</sub>, dichloromethane, 3 days, rt; (B) LAH, THF, 5 days, room temperature; (C) chloroacetyl chloride, K<sub>2</sub>CO<sub>3</sub>, 24h, refluxing dichloromethane; (D) ethyl diphenylphosphinite, 150 °C, 40 h.

the amides were alkylated to form *N*-methylated tris-CMPO ligands. The synthesis of the tertiary amide derivative of the tris-CMPO ligand was rather challenging. Even though preparation of the secondary amines **14** via acylation of **6a** and **11b**, and LAH reduction of **13** was quite straightforward, the final acylation with *p*-nitrophenyl (diphenylphosphoryl)-acetate took prolonged periods in the case of **16a** and **16b**, presumably due to the steric congestion caused by the three arms. A modified two-step procedure<sup>20</sup> was employed involving acylation of the secondary amine with the chloroacetyl chloride and subsequent Arbusov reaction,<sup>41</sup> presented in Scheme 3. The reaction of chloroacetyl chloride with **14a** afforded an 85% yield of **15a**, and the same reaction with **14b** resulted in a 66% yield of **15b**. The final product of the Arbusov reaction between molecule **15a** and ethyl diphenylphosphinite resulted in a 70% yield of product **16a**, whereas the same reaction with **15b** gave product **16b** with a 57% yield.

As shown in Figure 7, the polar cavity of the ligand was replaced by hydrophobic interactions between three methyl groups located on the amidic nitrogens, which caused all three carbonyl oxygens to point outward. It was anticipated that such a structural alteration would not only enhance the solubility of the extractant in nonpolar solvents, as desired, but perhaps even improve the extractability of Ln(III) and An(III), because of the increased basicity of the carbonyl oxygens.

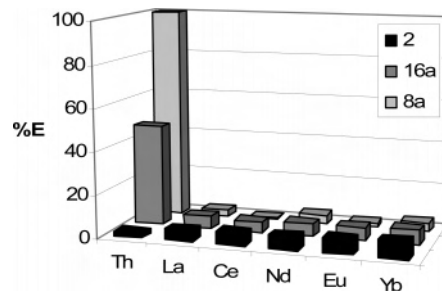
The alkylation of tris-CMPO has a significant impact on the extraction properties of the ligand. Surprisingly, both **16a** and **16b** showed lower selectivity for tetravalent thorium than their nonalkylated counterparts (**8a** and **12b**) (Chart 2).

In the solid-state structure of the Th(IV) complex with **8a** presented in Figure 3, the two nitrate anions are positioned at distances of 2.911 and 2.936 Å from the amide nitrogens, suggesting a weak hydrogen bonding interaction.<sup>28</sup> The decrease in the extraction ability for **16a** was especially pronounced in the case of Th(IV), for which the extraction was reduced over 50% with respect to the performance of the nonalkylated extractant **8a** (Chart 2). In the case of the



**Figure 7.** Diagram of the solid-state structure of **16a** (30% probability ellipsoids for nitrogen, oxygen, and phosphorus atoms; carbon atoms drawn with arbitrary radii). For clarity, all of the hydrogen atoms have been omitted.

**Chart 2.** Percent of Metal Extracted (%E) from 1 M Nitric Acid Solution by Mono-CMPO, **2**, Two-Carbon Linker Tris-CMPO, **8a**, and *N*-methylated Tris-CMPO, **16a**, Using 10<sup>-4</sup> M Metal Nitrate in 1 M Nitric Acid and 10<sup>-3</sup> M Ligand in Methylene Chloride



more-flexible ligand **16b**, a noticeable decrease of extraction (with respect to nonalkylated **12a**) along the entire series of studied metal ions was observed. As a result, *N*-alkylated **16a** (shorter CMPO tripod linker) and **16b** (longer CMPO tripod linker) display a similar selectivity profile. The complexity of the extraction process does not allow for an unambiguous explanation of such behavior, but if the nitrate counterions are bound via hydrogen bond interactions to the amidic hydrogens as was observed in the solid-state structures of the metal complexes, the presence of these hydrogens may be crucial for the transfer and stability of the complex in the organic phase.

**Examination of the Extraction Ability of 8a and 16b with Pu(IV).** The light actinides can be separated from the lanthanides because of the favored extractability of their higher oxidation states. Because the results of the extraction experiments have proven the ability of ligands **8a**, **b**, and **c** to take advantage of differences in oxidation states of tetravalent thorium and a series of trivalent lanthanides, we were prompted to study the extraction of the Pu(IV) ion, to verify the ability of the tris-CMPO molecule to preferentially extract tetravalent light actinides other than thorium. As outlined in Table 4, the tris-CMPO ligand was found to be highly effective for Pu(IV) separation, and the affinity for

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**Table 4.** Metal Extraction Percentages (%E)<sup>a</sup> for Pu(IV),<sup>b</sup> U(VI),<sup>b</sup> Am(III), and Eu(III) by Ligands: **8b**, **16a**, and **16b** in Methylene Chloride and 1-Octanol

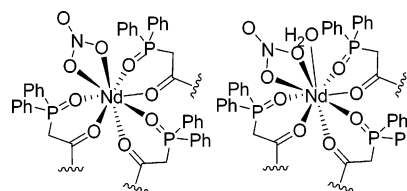
ligand	C <sub>L</sub>	solvent	Pu(IV), %E	U(VI), %E	Am(III), %E	Eu(III), %E
<b>8b</b>	10 <sup>-3</sup> M	CH <sub>2</sub> Cl <sub>2</sub>	98		27 <sup>c</sup>	29 <sup>c</sup>
<b>16a</b>	10 <sup>-3</sup> M	CH <sub>2</sub> Cl <sub>2</sub>	72	25		
<b>16b</b>	10 <sup>-3</sup> M	CH <sub>2</sub> Cl <sub>2</sub>	87	79		
<b>16b</b>	10 <sup>-2</sup> M	CH <sub>2</sub> Cl <sub>2</sub>	97	83	29	17
<b>16b</b>	10 <sup>-2</sup> M	1-octanol	86	61	6	3

<sup>a</sup> The metal solutions were spiked with the gamma nuclides to provide counting statistics for each sample within ~1% error. <sup>b</sup> Pu(IV) 10<sup>-5</sup> M, U(VI) 10<sup>-4</sup> M in 1 M HNO<sub>3</sub>. <sup>c</sup> 1M HNO<sub>3</sub>/5M NaNO<sub>3</sub>.

the 3+ metals was negligible. After 24 h of extraction, a significant fraction of 98% of Pu(IV) was removed from the aqueous phase by **8b** at concentrations as low as 10<sup>-3</sup> M, whereas the percent of metal extracted for all of the lanthanides was quite low. Even after only 30 min of extraction, almost all (96%) of the Pu(IV) is removed from the acidic solution (Table 4). In the industrial TRUEX process, high extraction values are obtained with very large concentrations of both mono-CMPO (0.2M) and TBP (1.2M),<sup>14,42</sup> and this results in the production of a large amount of secondary phosphorus waste that cannot be destroyed by incineration. Dramatically reducing the concentration of mono-CMPO, **2**, in solution results in a significant decrease in binding affinity for An(IV), as outlined in Chart 2. With a 30 equiv excess of ligand, the amount of metal extracted by **2** in the case of for the extraction of Th(IV) was ~2%, whereas under identical conditions with 10 equiv of **8a**, Th(IV) was almost completely removed from the acid layer. With the significant increase in affinity afforded by the preorganization of the three arms in the tris-CMPO complex, significant metal loading can be achieved in the organic layer with a much lower concentration of extractant in comparison to the TRUEX system, and no TBP coextractant would be required, potentially offering a considerable reduction in waste production.

As was noted in the Th(IV) extraction experiments (Chart 2), the *N*-alkylated ligand, **16a**, was not as effective for the extraction of Pu(IV) in comparison the simple tris-CMPO compound, **8b**. Upon amide alkylation, the percent of metal extracted into the organic layers dropped significantly from 98 to 72% at 10<sup>-3</sup> M ligand concentration in dichloromethane. However, a 10-fold increase in ligand concentration with the *N*-alkylated, three-carbon linker compound, **16b**, restores the high extraction value for Pu(IV) in the organic phase. Interestingly, a similar but more-dramatic decrease in extraction efficiency was noted with CMPO bearing calix-[*n*]arenes upon alkylation of the amide nitrogens.<sup>22</sup>

**Examination of the Extraction Ability of 8a and 16b with U(VI) and An(III).** In the early 1950s, Seaborg and co-workers<sup>43</sup> found that trivalent lanthanides and actinides

**Figure 8.** Diagrams of the cocrystallized neodymium(III) complexes of **8b**, anhydrous 8-coordinated +2 cationic complex (left) and water-containing 9-coordinated +2 cationic complex (right) from ref 28.

could be separated using cation-exchange resin columns because of the ability of the actinides to employ 5f orbitals in bonding, as discussed in the introduction. With these issues in mind, the Am(III)/Eu(III) extraction experiment was performed to test the ability of **8b** to take advantage of such a discrepancy between Am(III) and the similarly sized Eu(III) ion (Table 4). It was found, however, that **8b** has a very low affinity for both ions (%E less than 20), and it is not able to distinguish between these two elements. Upon enrichment of the aqueous phase with sodium nitrate, the ability of the ligands to extract americium and europium from the acidic layer slightly improved, as expected, but neither the extraction percentages nor the separation factor was satisfactory. In the case of the U(VI), both **8b** and **16b** showed moderate affinity, and in view of the structure of the uranyl ion, it is difficult to see how all three arms could simultaneously bind to the metal during the extraction event.

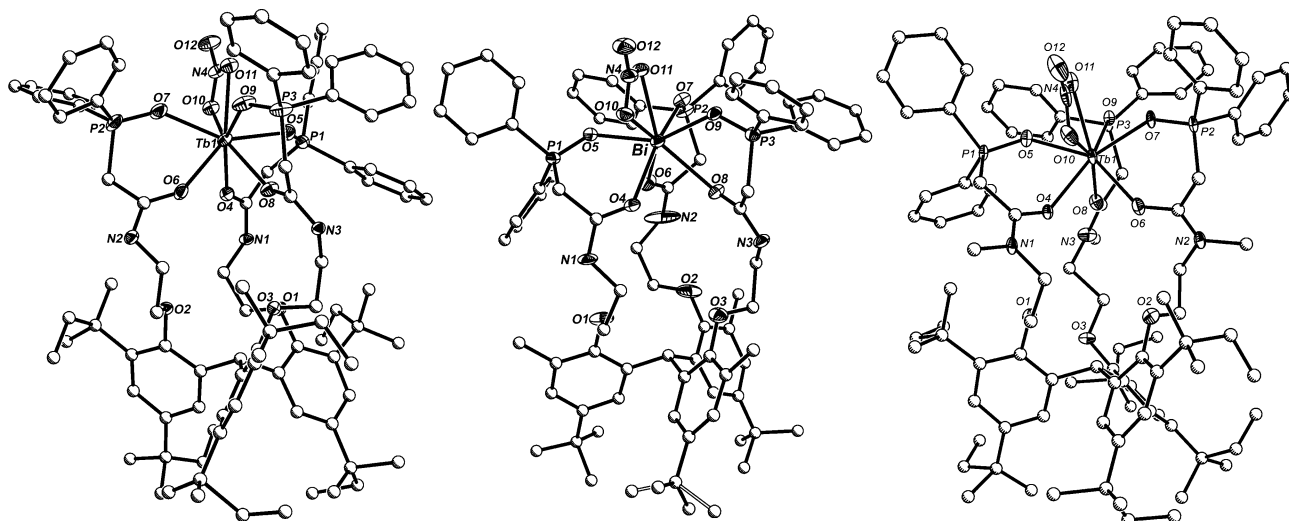
**Utilization of the Industrially Friendly Solvent 1-Octanol.** For real-world applications, dichloromethane would be a very poor choice for an extraction solvent because all of the problems associated with its use on an industrial scale. Accordingly, the extraction behavior of the most-soluble tris-CMPO compound, the *N*-methylated, three-carbon linker ligand, **16b**, was examined in 1-octanol. As it was observed in the case of CMPO-like calixarenes,<sup>44</sup> the binding potential of **16b** was somewhat mitigated in 1-octanol. At the same molar concentration of ligand **16b** in both solvents, the affinity for metal ions was much lower in 1-octanol than in dichloromethane (Table 4). In 1-octanol, the hydrogen bonding interactions between the solvent and the phosphoryl and carbonyl oxygens of the extractant may mitigate the extraction either by preventing ligand–metal binding or by simply changing the stability of the complex in the organic phase. Efforts to determine the true structure of the extracted species with both alkylated and nonalkylated ligands in solution, which would allow for better understanding of the extraction behavior of the ligands, are in progress.

**Solid-State Structures of Tris-CMPO Ligands with M(III) Ions.** The solvent extraction separation process is based on the transfer of a metal cation from an aqueous phase into an immiscible organic phase with simultaneous charge neutralization.<sup>5</sup> As we have previously shown in organic solvents,<sup>28</sup> the three CMPO arms in ligand **8b** tightly wrap around Ln(NO<sub>3</sub>)<sub>3</sub> (Ln = Eu(III), Nd(III)) in a bidentate fashion, forcing two of the nitrate counterions out of the

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**Figure 9.** Diagram of the structure of compounds **[8a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>** (left), **[8c·BiNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>** (center) and **[16a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>** (30% probability ellipsoids for M(III), nitrogen, oxygen, and phosphorus atoms; carbon atoms drawn with arbitrary radii). All of the hydrogen atoms and the disorder in the *tert*-pentyl groups have been omitted for clarity. In the solid state, **[8c·BiNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>** contained two complexes in the asymmetric unit and only one of the two essentially identical compounds is shown.

coordination sphere of the metal and producing a complex with an overall 2+ charge. In the solid-state structure of the Nd(III) species with **8b**, originally presented in ref 28, two distinct Nd(III) complexes cocrystallized (Figure 8). One metal center is eight coordinate, whereas the other Nd(III) contains an extra coordinated water molecule. As expected, all of the metal–oxygen bond lengths are slightly longer in the 9-coordinate species.

Similar, although only 8-coordinate structures were obtained for Tb(III) complexes with new derivatives of tris-CMPO chelates **8a** and **16a** and Bi(III) complex with **8c** (Figures 9), unlike Tb(III) complexes, the Bi(III) compound contained two similar structures in the asymmetric unit. Bismuth was chosen as a model for other large 3+ metal cations. In addition to solid-state structure analysis, the affinity of ligands **8b** and **8c** toward trivalent bismuth was tested to ensure selectivity of the tris-CMPO chelate over other f-element trivalent metal ions present in waste. The extractability of Bi(III) was found to be as low as that of the trivalent lanthanides. At the 10-fold excess of ligands **8b** or **8c** in dichloromethane, only 8% of bismuth was transferred to the organic phase.

In the solid-state structures, the different radii<sup>45</sup> of the studied metals (trivalent neodymium, terbium, and bismuth) were reflected in the variations of the bond lengths in the resulting complex. In the smallest, and therefore the most electropositive 8-coordinate Tb(III) ( $r = 1.180 \text{ \AA}$ ), the distances to the binding atoms are shorter than those in the 8- ( $r = 1.249 \text{ \AA}$ ) and 9- ( $r = 1.303 \text{ \AA}$ ) coordinate Nd(III) and that in the 8-coordinate Bi(III) ( $r = 1.310 \text{ \AA}$ ). In all of the cases, the metal–phosphoryl oxygen distance is shorter than the metal–carbonyl distance (P=O–M: **[16a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>**: 2.297(7)–2.322(6), **[8a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>**: 2.300(4)–2.315(5), Nd CN = 8: 2.394(9)–2.452(9), Nd CN = 9: 2.429(9)–2.436(10), Bi(1): 2.315(6)–2.414(6), Bi(2): 2.330(6)–2.394(6); C=O–M: **[16a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>**: 2.326(8)–

**Table 5.** Time Dependence on Extraction of a  $10^{-5} \text{ M}$  Solution of Pu(IV) by a  $10^{-3} \text{ M}$  Solution of **8b** in Methylene Chloride

time (hours)	Pu(IV), %E
<b>0.5</b>	96
<b>3</b>	98
<b>24</b>	98

2.373(7), **[8a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>**: 2.347(4)–2.397(4), Nd CN = 8: 2.358(9)–2.437(9), Nd CN = 9: 2.430(10)–2.490(10), Bi(1): 2.444(7)–2.575(6), Bi(2): 2.464(6)–2.533(6)).

The bond lengths between metal and the coordinated nitrate also follow the trend: Tb > Nd CN = 8 > Nd CN = 9 > Bi (**[8a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>**: 2.468(4)–2.480(4), **[16a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>**: 2.474(8)–2.599(5), Nd CN = 8: 2.535(10)–2.552(10), Nd CN = 9: 2.615(10)–2.621(10), Bi(1): 2.444(6)–2.519(6), Bi(2): 2.458(5)–2.587(6)). The Bi–O separation in this 8-coordinate compound was found to be somewhat longer from the average Bi–O distance in the neutral 8- and 9-coordinate bismuth nitrate complexes with tridentate 2,6-bis(–CH<sub>2</sub>–P(=O)R<sub>2</sub>) pyridine oxides [CN = 8 (2.321 Å); CN = 9 (2.340 Å)],<sup>46</sup> and similar to the distances in the 9-coordinate nitrate complex with (*i*PrO)<sub>2</sub>–(O)PCH<sub>2</sub>P(O)(O*i*Pr)<sub>2</sub> [2.432(2)–2.544(2) Å].<sup>47</sup>

The incorporation of the tertiary amide into the ligand scaffold seems to have a small influence on the terbium coordination environment in the solid-state complexes. The distances between phosphoryl oxygens and terbium ions in **[8a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>** and **[16a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>** are within the same range. The carbonyl oxygens and metal bond lengths are only slightly shorter in the **[16a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>** complex, but the nitrate is bound slightly weaker. Selected bond lengths of the molecular structures of **12b**, **16a**, **[8a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>**, **[16a·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>**, and **[8c·BiNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>** determined by the single-crystal X-ray diffraction analysis are summarized in Table 6.

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**Table 6.** Selected Bond Lengths (Angstroms) for **12b**, **16a**, [**8a**·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>, [**16a**·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>, and [**8c**·BiNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>

	<b>12b</b>	<b>16a</b>	[ <b>8a</b> ·TbNO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	[ <b>16a</b> ·TbNO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	[ <b>8c</b> ·BiNO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> Bi(1)	[ <b>8c</b> ·BiNO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> Bi(2)
P(1)–O(5)		1.480(3)	1.502(5)	1.505(7)	1.497(6)	1.506(6)
P(2)–O(7)		1.485(3)	1.497(5)	1.510(7)	1.502(7)	1.520(7)
P(3)–O(9)		1.484(3)	1.503(5)	1.520(7)	1.497(6)	1.498(7)
P(1)–O(3)	1.477(3)					
C(19)–O(2)	1.232(4)					
C(53)–O(4)		1.230(4)		1.289(12)		
C(70)–O(6)		1.233(4)		1.260(11)		
C(87)–O(8)		1.231(4)		1.240(12)		
C(52)–O(4)			1.261(7)			
C(68)–O(6)			1.232(8)			
C(84)–O(8)			1.248(7)			
			Metal–Phosphoryl			
M–O(5)			2.315(5)	2.322(6)	2.315(6)	2.352(5)
M–O(7)			2.308(5)	2.315(7)	2.334(6)	2.330(6)
M–O(9)			2.300(4)	2.297(7)	2.414(6)	2.394(6)
			Metal–Carbonyl			
M–O(4)			2.347(4)	2.326(8)	2.450(6)	2.464(6)
M–O(6)			2.349(5)	2.368(7)	2.444(7)	2.469(7)
M–O(8)			2.397(4)	2.373(7)	2.575(6)	2.533(6)
			Metal–Nitrate			
M–O(11)			2.468(4)	2.599(9)	2.444(6)	2.458(5)
M–O(10)			2.480(4)	2.474(8)	2.519(6)	2.587(6)

The nitrate counterions in the solid-state structures of both [**8a**·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> and [**8c**·BiNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> maintain hydrogen bonding interactions with the amide hydrogens. For example, the N–O distances range from 2.857(9) to 2.920(5) Å in [**8a**·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>. In contrast, the alkylated nitrogens in ligands **16a** and **16b** do not present suitable hydrogen bond donors to interact with the counterions, and during the extraction event, a charge separated complex would have to dissolve in the organic layer when the three CMPO arms wrap around the 4+ metal center. With **8b**, the hydrogen bonding interactions between the amides and nitrates could facilitate dissolution of the charged metal complex in the organic layer as discussed above, and the lack of these contacts may help explain the dramatic decrease in the extraction efficiency for An(IV) of **16a** and relative to **8a** outlined in Chart 2. Interestingly, reasonable extraction efficiency can be obtained with **16b** by increasing the ligand/metal ratios by a factor of 10, and without the alkylation of the ligand, these high ratios cannot be achieved with these large ligands because of the relatively poor solubility of **8a** in comparison to **16b**.

## Conclusions

A series of molecules containing three precisely arranged carbamoylmethylphosphine oxide (CMPO) moieties have been synthesized, and their ability to selectively extract actinides from simulated acidic nuclear waste streams has been evaluated. The ligand system has shown an excellent binding efficiency for An(IV) and Pu(IV) in particular at very low concentrations of ligand to metal. The preorganization of the arms and the large entropy increase afforded by a single ligand produces a very highly efficient and selective system for extraction of An(IV) from 1 M HNO<sub>3</sub>, particularly in comparison to the TRUEX system.<sup>14</sup> For example, 98% of Pu(IV) was removed from the acid phase by **8a** at concentrations of 10<sup>-3</sup> M (100:1 L/Pu(IV), ap-

proximately 1.5 grams of ligand per liter), whereas the extractions values for lanthanides were low. In the industrial TRUEX process, efficient extraction is normally obtained with very large concentrations of both mono-CMPO (0.2 M, 78 grams of CMPO per liter) and TBP (1.2M, 266 grams of TBP per liter).

As in the case of calix[4]arene and resorcinarene derivatives, the extraction efficiency of classic (*N,N*-diisobutylcarbamoylmethyl) octylphenylphosphineoxide (CMPO) extractant was notably improved by the attachment of CMPO-like functions on the triphenoxymethane skeleton. The unique geometrical arrangement of the three ligating groups, as opposed the four groups utilized in calix[4]arenes, enhanced the selectivity profile of this multi-CMPO extractant. To the best of our knowledge, the tris-CMPO ligands are among the most effective and selective CMPO-based ligands at low ratios of metal/ligand concentrations for the selective recognition of tetravalent actinides. The structural modifications of tris-CMPO have shown a significant decrease in the extraction efficiency and selectivity with the introduction of a tertiary amide into the ligand structure, presumably due to the lack of hydrogen bond donors to the nitrate counterions. Elongation of the secondary amide ligating arm slightly enhanced the extractability of all of the studied ions without a major reduction in selectivity, whereas a decrease in the number of chelating arms from three to two produced a very ineffective ligand highlighting the significance of the presence of exactly three preorganized chelating moieties for the efficient metal binding. This remarkable attraction for tetravalent actinides can be attributed to the match between coordination requirements of An(IV) and the geometrical environment presented by the ligand. Moreover, the higher charge density of tetravalent actinides with respect to trivalent f-elements may additionally account for the increased affinity of the tris-CMPO for An(IV) and the complex stability. Although the separation of Pu(IV) from An(III) and Ln(III)

is not a particularly difficult problem, the results with ligand **8** and **16** demonstrate that a properly designed, single-ligand system can achieve very high selectivity and binding efficiency for the actinides, and minor modification of the framework can result in large changes in both binding affinity and selectivity.

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**Supporting Information Available:** Disordered solvents removed from the data for **12a**, **16a**, [**8a**·TbNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>, and [**8c**·BiNO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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