

Synthesis and Coordination Properties of New Bis(phosphinomethyl)pyridine *N,P,P'*-Trioxides

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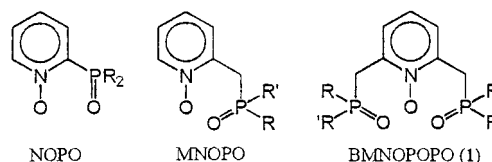
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In a search for more hydrocarbon solvent soluble derivatives of the parent ligand, 2,6-[Ph₂P(O)CH₂]₂C₅H₃NO (**1a**), a series of new ligands, 2,6-[R₂P(O)CH₂]₂C₅H₃NO [R = Bz (**1b**); Tol (**1c**); Et (**1d**); Pr (**1e**); Bu (**1f**); Pn (**1g**); Hx (**1h**); Hp (**1i**); and Oct (**1j**)] and 2,6-[RR'P(O)CH₂]₂C₅H₃NO [R = Ph, R' = Bz (**2a**); R = Ph, R' = Me (**2b**); R = Ph, R' = Hx (**2c**); R = Ph, R' = Oct (**2d**)], have been prepared by either Arbusov or Grignard substitutions on 2,6-bis(chloromethyl)pyridine followed by N-oxidation. The new ligands have been characterized by spectroscopic methods, and their coordination chemistry with selected lanthanide ions has been surveyed. Several 1:1 and 2:1 ligand/metal complexes have been isolated, and single-crystal X-ray diffraction analyses for Nd(**2a**)(NO₃)₃, Er(**2a**)(NO₃)₃, Yb(**1d**)(NO₃)₃, and [Nd(**1c**)₂](NO₃)₃ are described. The new structural data are discussed in relation to the structures of complexes formed by **1a**.

Introduction

The molecular design and synthesis of simple ligands that selectively chelate f-element ions over main group and transition metal species represent a critical area of research need. Due to the complex hydrolysis characteristics of f-element ions in neutral or weakly acidic aqueous solutions, it is necessary to develop chelators that are stable and functional in strongly acidic solution. This turns out to be a nontrivial task. In this regard, carbamoylmethylphosphonates (CMP) and carbamoylmethylphosphine oxides (CMPO) have previously been found to selectively coordinate with trivalent f-element ions present in highly acidic (>3 M HNO₃) solutions, and extraction ratios ($D = [M]_{\text{org}}/[M]_{\text{aq}}$) increase with increasing acid concentration. This unique behavior has led to the use of CMPO ligands in analytical and process liquid–liquid extraction (LLE) applications involving nuclear materials.¹ Recently, our group has reported the synthesis of a second family of robust ligands that include phosphinopyridine *N,P*-dioxides (NOPO), (phosphinomethyl)pyridine *N,P*-dioxides (MNOPO), and bis(phosphinomethyl)pyridine *N,P,P'*-trioxides (BMNOPOPO) (**1**).^{2–8} Crystallo-

graphic studies have shown that **1a** (R = R' = Ph)⁹ forms 1:1 and 2:1 ligand/metal complexes in which the ligand binds in a tridentate fashion with lanthanide(III) ions, Th(IV)⁵ and Pu(IV).⁸ In the 2:1 complexes, neutral **1a** partially displaces inner sphere



nitrate anions to the outer sphere. Ligand **1a** is soluble in CHCl₃, and liquid–liquid extractions of Ln(III) ions⁷ and Am(III)^{10,11} in HNO₃ and HCl solutions reveal that **1a** is an improved extractant compared to CMP and CMPO ligands under similar conditions. This is a very positive result; however, it is undesirable to employ CHCl₃ as the organic diluent in an LLE process. As a result, we have set out to prepare derivatives of **1** that would be soluble in hydrocarbon solvents yet would still display favorable chelation behavior and forward- and back-extraction kinetics for trivalent f-element ions. We report here the synthesis of a new group of ligands as well as aspects of their coordination chemistry that impact the development of a molecular level understanding of the function of these ligands as selective extractants.

Experimental Section

General Information. The organic reagents used in the syntheses were purchased from Aldrich Chemical Co., and organic solvents were obtained from VWR and dried by standard procedures. The lanthanide

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- (9) The abbreviations used in the text for organic substituents include Me = methyl, Et = ethyl, Pr = *n*-propyl, Bu = *n*-butyl, Pn = *n*-pentyl, Hx = *n*-hexyl, Hp = *n*-heptyl, Oct = *n*-octyl, Ph = phenyl, Bz = benzyl, and Tol = tolyl.
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nitrate salts were purchased from Ventron. All reactions were performed in Schlenk-style airless glassware under a dry nitrogen gas atmosphere unless noted otherwise. Infrared spectra were recorded on a Mattson 2020 FTIR instrument, and NMR spectra were obtained from Bruker FX-250 and JEOL GSX-400 spectrometers using Me₄Si (¹H, ¹³C) and 85% H₃PO₄ (³¹P) as shift standards. All downfield shifts from the reference were designated as +δ. The mass spectra were obtained at the Midwest Center for Mass Spectrometry, University of Nebraska, and elemental analyses were acquired at UNM or Galbraith Laboratories.

Ligand Syntheses. 2,6-Bis(chloromethyl)pyridine was prepared as described previously.⁶ **CAUTION:** Handling of this reagent and its solutions should be done in a well-ventilated hood. Skin and eye contact should be carefully avoided since the compound is an aggressive skin irritant toward some people. It also has a small vapor pressure at 23 °C and can cause bronchial irritation. We find that there is considerable variation in the intensity of effect on individuals by this compound, so great care should be employed with its handling.

2,6-Bis[(dibenzylphosphino)methyl]pyridine *N,P,P'*-Trioxide (1b). In a nitrogen-purged flask fitted with a reflux condenser, ethanol (46.0 g, 1.0 mol) was added dropwise with stirring to PCl₃ (137.4 g, 1.0 mol) at -70 °C (5 h).¹² After completion of the addition, the reaction mixture was stirred at 23 °C (2 h), during which time copious quantities of HCl vented through the reflux condenser and gas bubbler. The resulting mixture was distilled under reduced pressure, and (EtO)PCl₂ (63.0 g, 42.9%) was collected at 51–52 °C/90 mTorr as a colorless liquid. A sample of (EtO)PCl₂ (14.7 g, 0.1 mol) in Et₂O (100 mL) was cooled in an ice bath, and benzylmagnesium chloride (0.2 mol in Et₂O) was added dropwise (2 h). A white solid (MgCl₂) formed immediately. The resulting mixture was warmed to 23 °C, stirred for 2 h, and then allowed to stand overnight at 23 °C. The solution was filtered and the filtrate evaporated, leaving a liquid, which was vacuum distilled (75–80 °C/150 mTorr). The colorless distillate is Bz₂P(OEt) (11.8 g, 45.7%), ³¹P{¹H} δ 129.9. Under dry nitrogen, a sample of Bz₂P(OEt) (5.9 g, 0.023 mol) and 2,6-bis(chloromethyl)pyridine (2.0 g, 0.011 mol) were combined in triglyme (30 mL), and the mixture was refluxed (3 h, 150 °C, 20 mTorr). The EtCl produced was allowed to escape through the reflux condenser and bubbler, and a white solid formed. The resulting mixture was cooled (-12 °C, 30 min) and then filtered. The solid product was washed with cold Et₂O (3 × 10 mL), leaving a white solid, 2,6-bis(dibenzylphosphinomethyl)pyridine *P,P'*-dioxide (**3b**): yield 4.4 g, 66.7%. IR spectrum (KBr, cm⁻¹): 1192 (s, ν_{PO}). NMR spectra (CDCl₃): ³¹P{¹H} δ 41.8. A sample of **3b** (1.0 g, 1.8 mmol) in glacial acetic acid (5 mL) was combined with H₂O₂ (30% solution, 0.4 mL) and heated to 60–65 °C under dry nitrogen (16 h). An additional sample of H₂O₂ (0.4 mL) was then added and the reaction continued (2 h). The volatile contents were then evaporated in vacuo at 23 °C, water (3 mL) was added to the residue, and the volatiles again were evaporated. The remaining white residue was dissolved in CHCl₃ (15 mL) and extracted with saturated aqueous NaHCO₃ solution (15 mL) and the aqueous phase extracted with CHCl₃ (2 × 10 mL). The combined CHCl₃ solution containing the product was washed with fresh water (5 mL) and dried over anhydrous Na₂SO₄. The dried solution was recovered and evaporated in vacuo, leaving white solid **1b**: yield 1.0 g, 97%; mp 185–186 °C; soluble in CHCl₃, benzene (1 × 10⁻² M), and toluene (3 × 10⁻³ M). Anal. Calcd for C₃₅H₃₅N₃O₃P₂: C, 72.53; H, 6.09; N, 2.42. Found: 72.91; H, 5.89; N, 2.40. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 580.4 (M + H⁺) [100], 579.4 (M⁺) [10], 564.4 (M + 1 - O⁺) [7], 488.3 (M - PhCH₂⁺) [10]. IR spectrum (KBr, cm⁻¹): 1232 (s, ν_{NO}) 1176 (s, ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 41.7.

2,6-Bis[(ditolylphosphino)methyl]pyridine *N,P,P'*-Trioxide (1c). A solution of diethyl phosphite (6.08 g, 0.044 mol) in dry diethyl ether (10 mL) and benzene (30 mL) was added dropwise (2 h) with stirring to *p*-tolylmagnesium bromide (132 mL, 1 M solution in Et₂O; 0.132 mol) at 23 °C. The temperature of the solution rose during the addition, and the mixture was refluxed at 60–70 °C (1.5 h) following completion

of the addition. A yellow colloid-like material formed. The mixture was cooled to 23 °C, and 2,6-bis(dichloromethyl)pyridine (3.52 g, 0.02 mol) in dry benzene (20 mL) was added. Reflux (1 h) produced a brown greasy product and an orange solution, which was decanted. The brown oil was treated with a mixture of saturated aqueous NH₄Cl (100 mL) and CHCl₃ (60 mL), the layers were separated, and the aqueous phase was washed with CHCl₃ (2 × 40 mL). The combined CHCl₃ phase was washed with water (20 mL) and then dried with anhydrous Na₂SO₄. Vacuum evaporation of the solvent gave 2,6-bis(ditolylphosphinomethyl)pyridine *P,P'*-dioxide (**3c**) as an orange solid: yield 10.8 g, 95.8%. IR spectrum (KBr, cm⁻¹): 1182 (s, ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 31.3. A sample of **3c** (10.8 g, 19 mmol) in glacial acetic acid (50 mL) was treated with 30% H₂O₂ (4.4 mL, 30 mmol) and the solution heated to 65 °C (15 h) under nitrogen. An additional aliquot of H₂O₂ (4.4 mL) was then added and heated for an additional period (2 h). The volatiles were removed by vacuum evaporation at 23 °C and the residue treated with water (10 mL) and then dried in vacuo. The residue was dissolved in CHCl₃ (70 mL), and this was extracted with saturated aqueous NaHCO₃ (70 mL). The water phase was separated and treated with CHCl₃ (2 × 30 mL). The combined CHCl₃ phases were washed with water (30 mL) and dried over Na₂SO₄. The solution was evaporated in vacuo and the residue washed with Et₂O (3 × 20 mL), leaving a white solid, 2,6-bis(ditolylphosphinomethyl)pyridine *N,P,P'*-trioxide (**1c**): yield 9 g, 81%; mp 187–188 °C; soluble in CHCl₃ and benzene (6 × 10⁻² M). Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 580.2 (M + 1⁺) [100], 579.2 (M⁺) [10], 488.1 (M - C₆H₄CH₃⁺) [10]. IR spectrum (KBr, cm⁻¹): 1236 (s, ν_{NO}), 1184 (s, ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 32.1.

2,6-Bis[(diethylphosphino)methyl]pyridine *N,P,P'*-Trioxide (1d). A sample of ethylmagnesium bromide (44 mL, 3 M solution in Et₂O, 0.13 mol) was added to THF (65 mL) under dry nitrogen, and the flask was briefly purged to remove the majority of the Et₂O. To this solution was added dropwise (EtO)₂P(O)H (6.08 g, 0.044 mol) in dry benzene (30 mL) (2 h). The temperature rose during the addition, and at the end the mixture was refluxed (1 h, 75 °C), and then 2,6-dichloromethylpyridine (3.52 g, 0.02 mol) in benzene (20 mL) was added at 23 °C. This mixture was refluxed (5.5 h), and then volatiles were evaporated. The orange residue was treated with saturated aqueous NH₄Cl (100 mL) and then extracted with CHCl₃ (6 × 60 mL). The combined CHCl₃ extracts were dried (Na₂SO₄) and then evaporated. The resulting residue was washed with cold Et₂O (10 mL), leaving a white solid, bis(diethylphosphinomethyl)pyridine *P,P'*-dioxide (**3d**): yield 4.6 g, 73.7%. IR spectrum (KBr, cm⁻¹): 1153 (ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 50.2. A sample of **3d** (4.4 g, 13.9 mmol) was N-oxidized as described for **3c**, and the workup was similar. The product, 2,6-bis(diethylphosphinomethyl)pyridine *N,P,P'*-trioxide (**1d**) was isolated as a white solid: yield 3.4 g, 73.8%; mp 110–111 °C; soluble in CHCl₃, benzene (1.5 × 10⁻¹ M), toluene (4 × 10⁻² M), and xylene (2 × 10⁻² M). Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 332.1 (M + 1⁺) 100%, 331.1 (M⁺) 5%, 316.1 (M + 1-O⁺) 10%, 274.1 (M + 1-2(Et)⁺) 5%. IR spectrum (KBr, cm⁻¹): 1248 (s, ν_{NO}), 1161 (s, ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 51.4.

2,6-Bis[(di-*n*-propylphosphino)methyl]pyridine *N,P,P'*-Trioxide (1e). This compound was prepared as described for **1d** using *n*-propylmagnesium chloride. The intermediate **3e** was obtained as a white solid: yield 6.6 g, 88.2%. IR spectrum (KBr, cm⁻¹): 1157 (s, ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 47.3. The N-oxidation of **3e** was performed as described for **3d**, and **1e** was obtained as a white solid: yield 5.5 g, 82.1%; mp 107–108 °C. Soluble in CHCl₃, benzene, toluene, and xylene. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 388.2 (M + H⁺) [100], 387.2 (M⁺) [3], 372.2 (M + 1 - O⁺) [10]. IR spectrum (KBr, cm⁻¹): 1257 (s, ν_{NO}) 1153 (s, ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 48.2.

2,6-Bis[(di-*n*-butylphosphino)methyl]pyridine *N,P,P'*-Trioxide (1f). This compound was prepared as described for **1d** using *n*-butylmagnesium chloride. The intermediate **3f** was isolated as a white solid: yield 6.0 g, 70%. IR spectrum (KBr, cm⁻¹): 1165 (s, ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 47.78. The N-oxidation of **3f** was done as described for **3d**, and **1f** was obtained as a white solid: yield 4.2 g, 84.1%; mp 73–74 °C; soluble in CHCl₃, benzene, toluene, and heptane. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 444.3 (M + H⁺)

(12) The synthesis of (EtO)PCl₂ has been reported in the literature, and the procedure employed here uses a slight variation: *J. Chem. Soc., Perkin Trans.* **1975**, 2, 1185.

[100], 443.3 (M^+) [3], 428.3 ($M + 1 - O^+$) [10]. Infrared spectrum (KBr, cm^{-1}): 1230 (s, ν_{NO}), 1159 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 48.7.

2,6-(Di-*n*-pentylphosphino)methylpyridine *N,P,P'*-Trioxide (1g). This compound was prepared similarly to **1d** using *n*-pentylmagnesium bromide. The intermediate **3g** was initially obtained as an oil that solidified as a tan solid upon standing at 23 °C. The solid was recrystallized by dissolution in hot hexane and cooling in an ice bath. The resulting white solid (**3e**) was washed with cold hexane: yield 6.8 g, 70.4%. IR spectrum (KBr, cm^{-1}): 1165 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ 47.7. The N-oxidation reaction was done as described for **3c**. Following drying of the $CHCl_3$ solution of crude **1g**, the solution was evaporated and the residue was treated with pentane (20 mL). The solution was cooled to -20 °C, and white solid **1g** formed, which was collected and washed with cold pentane (2×20 mL): yield 4.7 g, 81.3%; mp 69–70 °C; soluble in $CHCl_3$, benzene, toluene, xylene, heptane, and hexane. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 500.3 ($M + 1^+$) [100], 499.3 (M^+) [5], 484.3 ($M + 1 - O^+$) [10]. IR spectrum (KBr, cm^{-1}): 1234 (s, ν_{NO}), 1167 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 48.7.

2,6-Bis[(di-*n*-hexylphosphino)methylpyridine *N,P,P'*-Trioxide (1h). This compound was prepared as described for **1d** using *n*-hexylmagnesium bromide. The intermediate **3h** was obtained as an orange sticky oil: yield 10.3 g, 95.1%. IR spectrum (KBr, cm^{-1}): 1157 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 47.8. The N-oxidation was performed as described for **3d**. The $CHCl_3$ solution containing **1h** was dried over Na_2SO_4 and the $CHCl_3$ evaporated, leaving **1h** as a sticky oil. yield 8.2 g, 80.1%. This may be further purified by column chromatography on silica gel using MeOH/ $CHCl_3$ (2.5:100) as the eluant. The pure compound is a colorless waxy solid: mp 59–60 °C; soluble in $CHCl_3$, Et_2O , benzene, toluene, pentane, hexane, and heptane. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 556.4 ($M + 1^+$) [100], 555.4 (M^+) [5], 540.4 ($M + 1 - O^+$) [10]. Infrared spectrum (KBr, cm^{-1}): 1242 (s, ν_{NO}), 1159 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 48.7.

2,6-Bis[(di-*n*-heptylphosphino)methylpyridine *N,P,P'*-Trioxide (1i). This compound was prepared as described for **1d** using *n*-heptylmagnesium bromide which was prepared from heptyl bromide and Mg turnings in diethyl ether. The intermediate **3i** was redissolved in warm pentane (40 mL) and then allowed to stand at 5 °C (1 h). A white solid **3i** formed, which was washed with cold pentane: yield 8.5 g, 71.2%. IR spectrum (KBr, cm^{-1}): 1165 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 47.7. The N-oxidation proceeded as outlined for **1d**, and **1i** was isolated as a white solid: yield 6.9 g, 83.3%; mp 67–68 °C; soluble in $CHCl_3$, benzene, toluene, xylene, heptane, hexane, and pentane. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 612.5 ($M + 1^+$) [100], 611.5 (M^+) [5], 596.5 ($M + 1 - O^+$) [10]. Infrared spectrum (KBr, cm^{-1}): 1255 (s, ν_{NO}), 1159 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 48.9.

2,6-Bis[(di-*n*-octylphosphino)methylpyridine *N,P,P'*-Trioxide (1j). This compound was prepared as described for **1d** using *n*-octylmagnesium chloride. The intermediate **3j** was obtained as an orange sticky oil: yield 12.4 g, 95.1%. IR spectrum (KBr, cm^{-1}): 1165 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 47.3. The N-oxidation proceeded as described for **1d**, and crude **1j** was obtained as a sticky oil: yield 11.3 g, 89.0%. This was further purified by column chromatography on silica gel using MeOH/ $CHCl_3$ (3:100) as eluant. This provides **1j** as a waxy solid: mp 70–71 °C; soluble in $CHCl_3$, benzene, toluene, pentane, hexane, and heptane. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 668.5 ($M + 1^+$) [100], 667.5 (M^+) [7], 652.5 ($M + 1 - O^+$) [10]. Infrared spectrum (KBr, cm^{-1}): 1236 (s, ν_{NO}), 1157 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 48.9.

2,6-Bis[(benzylphenylphosphino)methylpyridine *N,P,P'*-Trioxide (2a). A mixture of freshly distilled $PhPCl_2$ (8.95 g, 0.05 mol) and diethylphenylphosphonite (10 g, 0.05 mol) in dry diethyl ether (100 mL) was refluxed (1 h). The solution was cooled (5 °C), and $BzMgCl$ (100 mL, 1 M solution in Et_2O , 0.1 mol) was added dropwise with stirring (1 h). The resulting mixture was allowed to stand overnight (23 °C), and then it was then filtered and the volatiles were removed by evaporation. Distillation (70–90 °C, 400 mTorr) gave ethyl benzylphenylphosphinite: yield 13 g, 53%. NMR spectrum ($CDCl_3$):

$^{31}P\{^1H\}$ δ 119.1. Samples of ethyl benzylphenylphosphinite (11 g, 0.045 mol) and 2,6-bis(chloromethyl)pyridine (3.52 g, 0.02 mol) were combined in dry triglyme (25 mL) and refluxed (150 °C, 20 mTorr, 3 h). During the reaction, white solid formed. The reaction mixture was cooled (23 °C) and the white solid (**4a**) collected by filtration and washed with cold Et_2O (3×20 mL): yield 4 g, 37%. An additional 7 g (65%) of crude, light orange solid **4a** was recovered by evaporation of the triglyme. IR spectrum (KBr, cm^{-1}): 1192 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 36.9. A sample of **4a** (1.00 g, 1.87 mmol) was dissolved in glacial acetic acid (5 mL), and H_2O_2 (30%, 0.4 mL) was added. The mixture was stirred at 60–65 °C under nitrogen (16 h). Additional H_2O_2 (0.4 mL) was added and the mixture heated (2 h). The solution was vacuum evaporated and the residue treated with H_2O (5 mL), vacuum dried at 40 °C, and then dissolved in $CHCl_3$ (15 mL). The $CHCl_3$ solution was extracted with saturated $NaHCO_3$ solution (15 mL), the water phase was washed with $CHCl_3$ (2×10 mL), and the $CHCl_3$ fractions were combined, washed with water (5 mL), and dried with Na_2SO_4 . The $CHCl_3$ was evaporated, leaving white solid **2a**: yield 1 g, 97%; mp 163–164 °C; soluble in $CHCl_3$. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 552.4 ($M + H^+$) [100], 551.4 (M^+) [10], 536.4 ($M + 1 - O^+$) [10]. IR spectrum (KBr, cm^{-1}): 1228 (s, ν_{NO}), 1184 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 36.5.

2,6-Bis[(methyl(phenyl)phosphino)methylpyridine *N,P,P'*-Trioxide (2b). Ethyl phenyl phosphinate (7.5 g, 0.044 mol) in dry Et_2O (10 mL)/benzene (30 mL) solution was added dropwise (1 h) to $MeMgBr$ (29.3 mL, 3 M solution in Et_2O , 0.088 mol). The temperature rose during the addition, and a white precipitate formed. The mixture was heated (1 h, oil bath 67 °C) and then cooled (23 °C), and 2,6-bis(chloromethyl)pyridine (3.5 g, 0.02 mol) in dry benzene (20 mL) was added. The resulting mixture was refluxed (4 h) and cooled (23 °C), and a pale yellow solid was collected by filtration. The solid was treated with aqueous NH_4Cl (sat.) (80 mL) and $CHCl_3$ (60 mL) in a separatory funnel. The organic and aqueous (pH = 7–8) phases were separated, the water phase was washed with $CHCl_3$ (2×30 mL), and the combined $CHCl_3$ phases were washed with water (30 mL). The $CHCl_3$ solution was dried over Na_2SO_4 , then decanted, and evaporated, and acetone (10 mL) added was to the pasty residue. The resulting solid (**4b**) was collected by filtration and washed with acetone (2×10 mL): yield 3.2 g, 42.1%. IR spectrum (KBr, cm^{-1}): 1192 (s, ν_{PO}). NMR spectrum: $^{31}P\{^1H\}$ δ 33.2. A sample of **4b** (3.0 g, 7.8 mmol) in glacial acetic acid (15 mL) was treated with H_2O_2 (30%, 1.2 mL, 11 mmol) (65 °C, 16 h) under nitrogen. An additional aliquot of H_2O_2 was then added (1.2 mL) and the mixture heated (2 h). The solution was evaporated (23 °C) and the residue treated with water (10 mL) and dried. The colorless residual oil was dissolved in $CHCl_3$ (20 mL), which was extracted with aqueous saturated $NaHCO_3$ solution (20 mL). The water phase was washed with fresh $CHCl_3$ (2×10 mL), and the combined $CHCl_3$ phases were washed with water (10 mL) and dried over Na_2SO_4 . The solution was decanted and evaporated under vacuum, and the solid was washed with ethyl acetate (3×5 mL), leaving a white solid **2b**: yield 1.7 g, 54%; mp 181–182 °C; soluble in $CHCl_3$, benzene, and toluene. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 400.1 ($M + 1^+$) [100], 399.1 (M^+) [5], 384.1 ($M - Me^+$) [15]. IR spectrum (KBr, cm^{-1}): 1253 (s, ν_{NO}), 1170 (s, ν_{PO}). NMR spectrum ($CDCl_3$): $^{31}P\{^1H\}$ δ 36.9.

2,6-Bis[(*n*-hexyl)(phenyl)phosphino)methylpyridine *N,P,P'*-Trioxide (2c). Phenylphosphinic acid (56.8 g, 0.4 mol) and triethyl phosphite (71.4 g, 0.43 mol) were stirred together (60 °C, 1 h) and then distilled under reduced pressure. Diethyl phosphite (51.6 g) (35 °C/80 mTorr) and ethyl phenylphosphinate (63.6 g) (77–78 °C/80 mTorr) were collected: yield 93%. A sample of ethyl phenylphosphinate (7.48 g, 0.044 mol) in dry Et_2O (8 mL) and benzene (30 mL) was added to hexylmagnesium bromide (44 mL, 2 M solution in Et_2O , 0.88 mol). The temperature of the mixture increased during addition, and the mixture was then heated with an oil bath (65 °C, 2 h). The mixture was cooled (23 °C), and 2,6-bis(chloromethyl)pyridine (3.52 g, 0.02 mol) in benzene (20 mL) was added. The mixture was refluxed with an oil bath (70 °C, 4 h) and then allowed to stand (23 °C, overnight). An orange upper layer formed, which was decanted, and saturated aqueous NH_4Cl (80 mL) and $CHCl_3$ (60 mL) were added to the lower layer. The organic and aqueous (pH: 7–8) layers were separated, and

Table 1. Crystallographic Data

	Er(2a)(NO ₃) ₃	Nd(2a)(NO ₃) ₃	Yb(1d)(NO ₃) ₃ ·Me ₂ CO	[Nd(1c) ₂ (H ₂ O) ₂](NO ₃) ₃ ·H ₂ O·2.5CH ₃ CN
empirical formula	C ₃₃ H ₃₁ ErN ₄ O ₁₂ P ₂	C ₃₃ H ₃₁ Nd ₄ NdO ₁₂ P ₂	C ₁₈ H ₃₃ N ₄ O ₁₃ P ₂ Yb	C ₁₂ H ₇₈ N ₆ NdO _{17.5} P ₄
fw	904.82	881.80	748.46	1575.52
<i>a</i> , Å	25.087(4)	24.766(7)	11.100(1)	15.133(4)
<i>b</i> , Å	13.563(1)	13.696(3)	19.096(2)	15.930(3)
<i>c</i> , Å	10.438(2)	10.532(2)	13.722(2)	19.947(5)
α , deg	90	90	90	68.35(2)
β , deg	90	90	95.37(1)	68.54(1)
γ , deg	90	90	90	81.42(2)
<i>V</i> , Å ³	3551.5(8)	3572(2)	2895.8(6)	4159(2)
space group	<i>Pna</i> 2 ₁	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i>	4	4	4	2
<i>D</i> _{calcd} , g/cm ³	1.692	1.640	1.717	1.258
μ , mm ⁻¹	2.521	1.611	3.405	0.765
R1, ^a wR2 ^b	0.0369/0.0820	0.0307/0.0625	0.0288/0.0611	0.0624/0.1654

the water phase was washed with CHCl₃ (2 × 30 mL). The combined CHCl₃ layers were washed with fresh water (20 mL) and dried over Na₂SO₄. The CHCl₃ was decanted and evaporated, and an orange sticky oil (**4c**) was obtained: yield 9.6 g, 92.1%. IR spectrum (KBr, cm⁻¹): 1182 (s, ν_{PO}). NMR spectrum: ³¹P{¹H} (CDCl₃) δ 39.1. The N-oxidation was performed as described for **4a**, and **2c** was obtained as a colorless sticky oil: yield 7.7 g, 88.3%. Further purification on a silica gel column with MeOH/CHCl₃ (2.5:100) eluant still resulted in an oil; soluble in CHCl₃, Et₂O, benzene, and toluene. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 540.3 (M + 1⁺) [100], 539.3 (M⁺) [5], 524.3 (M + 1 - O⁺) [15]. IR spectrum (KBr, cm⁻¹): 1242 (s, ν_{NO}), 1184 (s, ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 40.4.

2,6-Bis(*n*-octyl)(phenyl)phosphino)methylpyridine *N,P,P'*-Trioxide (2d**).** This compound was obtained in the same fashion as **2c**. The intermediate **4d** was prepared from the reaction of octyl(phenyl)phosphinomagnesium chloride and 2,6-bis(chloromethyl)pyridine, and it was isolated as an orange, sticky oil: yield 11.3 g, 97%. IR spectrum (KBr, cm⁻¹): 1182 (s, ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 39.4. The N-oxidation proceeds in the same fashion as the conversion of **4c** to **2c**, and **2d** is recovered as a colorless oil: 10.7 g, 94%; soluble in CHCl₃, Et₂O, benzene, and toluene. Mass spectrum (FAB) *m/e* (fragment) [rel int, %]: 596.3 (M + 1⁺) [100], 595.3 (M⁺) [5], 580.3 (M + 1 - O⁺) [20]. IR spectrum (KBr, cm⁻¹): 1244 (s, ν_{NO}), 1188 (s, ν_{PO}). NMR spectrum (CDCl₃): ³¹P{¹H} δ 40.5.

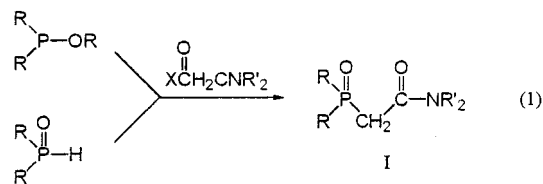
Preparation of Complexes. Ytterbium nitrate, Yb(NO₃)₃·5H₂O (360 mg, 0.8 mmol), and **1d** (265 mg, 0.8 mmol) were dissolved in acetone (25 mL) and stirred, and then the solvent was allowed to slowly evaporate at 25 °C. After 24 h, blocky crystals deposited and a suitable crystal was selected for single-crystal X-ray diffraction analysis. Similar recipes were used to prepare the other 1:1 complexes, and single crystals of Er(**2a**)(NO₃)₃ and Nd(**2a**)(NO₃)₃ were also prepared for crystallographic analysis. Neodymium nitrate, Nd(NO₃)₃·6H₂O (44 mg, 0.1 mmol), and **1c** (116 mg, 0.2 mmol) were dissolved in CH₃CN (15 mL) and stirred, and the solvent was allowed to slowly evaporate. After 2 weeks, purple crystals of suitable quality for X-ray crystallographic analysis were obtained.

X-ray Diffraction Analyses. Single crystals of Yb(**1d**)(NO₃)₃·Me₂CO (colorless plate, 0.69 × 0.46 × 0.12 mm), Er(**2a**)(NO₃)₃ (pale pink prism, 0.21 × 0.21 × 0.58 mm), Nd(**2a**)(NO₃)₃ (pale blue chip, 0.25 × 0.39 × 0.46 mm), and [Nd(**1c**)₂(H₂O)₂](NO₃)₃·H₂O·2.5 CH₃CN (colorless rod, 0.92 × 0.21 × 0.16 mm) were placed in glass capillaries and flame sealed. Data sets were collected on a Siemens R3m/V diffractometer equipped with a graphite monochromator and using Mo K α radiation (λ = 0.71073 Å). Lattice and data collection parameters are summarized in Table 1. All calculations were performed with SHELXTL PLUS (VMS version).¹³ The structure solution for [Nd(**1c**)₂(H₂O)₂](NO₃)₃·H₂O·2.5 CH₃CN was by direct methods while the

others employed Patterson methods. Full-matrix least-squares refinements,¹⁴ using appropriate neutral atom scattering factors and anomalous dispersion terms, included anisotropic thermal parameters for all atoms heavier than hydrogen. Data were corrected for absorption using empirical methods based on ψ scans. Some individual refinement details are provided. The refinements for Yb(**1d**)(NO₃)₃·Me₂CO, Er(**2a**)(NO₃)₃, and Nd(**2a**)(NO₃)₃ were well behaved, and hydrogen atoms were included in the final cycles of least-squares refinements in idealized positions calculated by the riding model with $U_{iso} = 1.25U_{equiv}$ of the parent atom. The refinement for [Nd(**1c**)₂(H₂O)₂](NO₃)₃·H₂O·2.5CH₃CN revealed that two of the outer-sphere nitrate ions (N(4)O₃ and N(5)-O₃) were disordered, and they were constrained as planes with N–O 1.24(1) Å. One CH₃CN was disordered over two sites, and these were set to half-occupancy. The phenyl groups were refined as rigid hexagons (C–C, 1.390 Å, and C–C–C, 120°). Selected bond distances are summarized in Table 2.

Results and Discussion

Arbusov and Michaelis–Becker reactions^{15,16} are typically used to prepare organophosphonates and phosphine oxides in moderate to good yields. The specific reaction route chosen for a target compound usually is governed by the commercial availability or ease of synthesis of the phosphite starting material. Gatrone and co-workers¹⁷ have reviewed the use of this chemistry to prepare a wide range of symmetric and asymmetric bis-aryl, bis-alkyl, and alkyl,aryl carbamoylmethylphosphine oxides (**I**, eq 1). It was expected that some of this



chemistry would be transferable to the synthesis of new bis-(phosphinomethyl)pyridine *N,P,P'*-trioxides (BMNOPOPO) **1**, and this has proven to be the case. For example, Michalski¹⁸ observed that a MNOPO derivative (R = R' = Ph) could be

(13) Sheldrick, G. M. *Nicolet SHELXTL Operations Manual*; Nicolet XRD Corp.: Cupertino, CA, 1981. SHELXTL uses absorption, anomalous dispersion, and scattering factor data compiled in the following: *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1970; Vol. 4, pp 55–60, 99–101, 149–150. Anomalous-dispersion terms were included for all atoms with atomic numbers greater than 2.

(14) A general description of the least-squares algebra is found in the following: *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; p 187. The least-squares refinement minimizes $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma(F)^2 + gF^2)$.

(15) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper and Row: London, 1976.

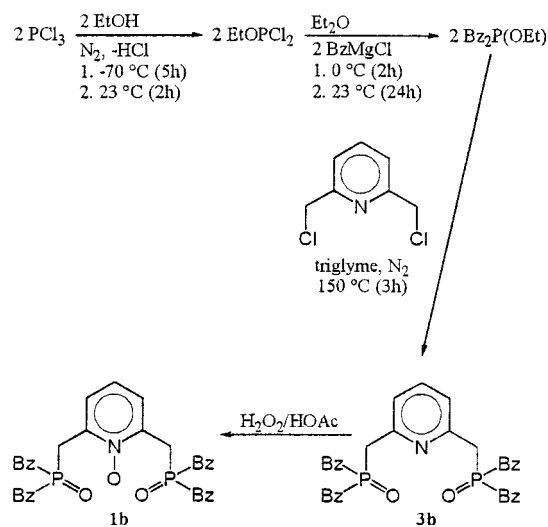
(16) Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley-Interscience: New York, 2000.

(17) Gatrone, R. C.; Kaplan, L.; Horwitz, E. P. *Solvent Extr. Ion Exch.* **1987**, *5*, 1075.

(18) Maruszewska-Wieczorkowska, E.; Michalski, J. *Rocz. Chem.* **1964**, *38*, 625.

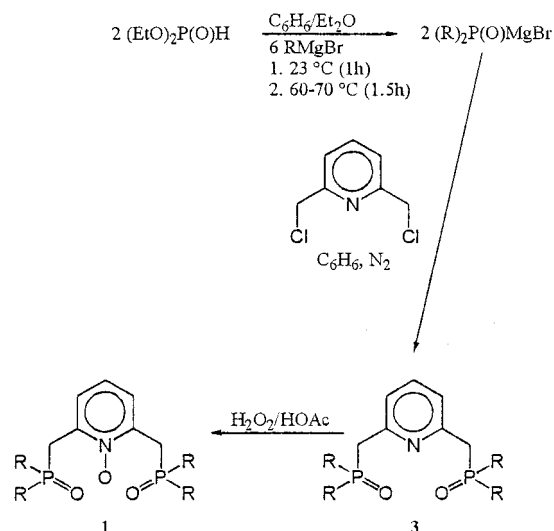
Table 2. Selected Bond Distances (Å)

bond	Er(2a)(NO ₃) ₃	Nd(2a)(NO ₃) ₃	Yb(1d)(NO ₃) ₃ ·Me ₂ CO	[Nd(1c) ₂ (H ₂ O) ₂](NO ₃) ₃ ·H ₂ O·2.5CH ₃ CN
M—O(P)	2.280(7)	2.390(3)	2.223(3)	2.394(6)
	2.281(6)	2.378(3)	2.233(3)	2.383(6)
M—O(N) _{pyr}				2.341(6)
	2.278(7)	2.382(3)	2.278(3)	2.383(6)
				2.507(6)
M—OH ₂				2.504(6)
				2.515(6)
M—O(N) _{nitrate}	2.453(7)	2.536(3)	2.309(3)	2.561(6)
	2.575(7)	2.599(3)	2.456(3)	
	2.375(6)	2.453(3)	2.413(4)	
	2.420(8)	2.534(3)	2.439(4)	
	2.444(7)	2.561(3)	2.520(3)	
	2.500(7)	2.567(3)	2.381(3)	
P=O	1.500(7)	1.500(3)	1.503(3)	1.487(6)
	1.498(6)	1.504(3)	1.503(3)	1.501(6)
N—O				1.508(6)
				1.493(3)
	1.352(10)	1.337(4)	1.341(4)	1.339(8)
				1.312(9)

Scheme 1

obtained from a Michaelis–Becker reaction between 2-(ClCH₂)-C₅H₄N and NaOPPh₂, and we reported that the same compound is formed in a metathesis reaction between 2-(ClCH₂)-C₅H₄N and KPPH₂ followed by phosphane oxidation with H₂O₂/EtOH solution.⁵ The 2,6-bis[(diphenylphosphino)methyl]pyridine *N,P,P'*-trioxide **1a** was initially prepared in our group by the metathesis reaction between 2,6-bis(chloromethyl)pyridine and KPPH₂ followed by H₂O₂/EtOH oxidation;⁵ however, this reaction is not easily extended to other R,R or R,R' combinations since many of the phosphane (RR'PH) starting materials are neither commercially available nor easily handled in large quantities. Subsequently, we reported that the precursor, **3a**, could be reliably made in large amounts by an Arbusov reaction employing Ph₂P(OEt); **3a** is efficiently oxidized (H₂O₂/HOAc) to give the desired *N,P,P'*-trioxide **1a** in 85% overall yield.⁶ These results and our need for additional derivatives of **1** with improved solubility in hydrocarbon solvents as well as modified donor strength led us to a broader study of the synthesis of derivatives of **3** and **1**.

The syntheses for the symmetrical BMNOPOPO (R = R') compounds **1b–j** are summarized in Schemes 1 and 2. In each case, the BMNOPOPO derivatives **3b–j** are also isolated. The procedure outlined in Scheme 1 involves an Arbusov reaction that is simple and easy to perform; however, the yield of **3b** is low (67%), and impurities generated during the thermally driven

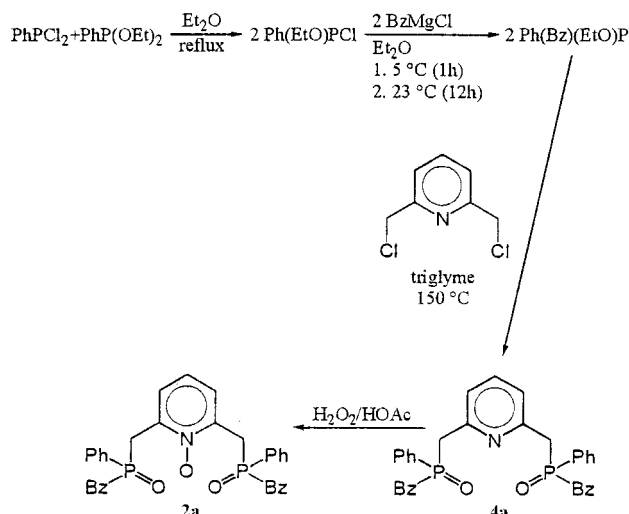
Scheme 2

	1c	1d	1e	1f	1g	1h	1i	1j
R	Tol	Et	Pr	Bu	Pn	Hx	Hp	Oc
	3c	3d	3e	3f	3g	3h	3i	3j
R	Tol	Et	Pr	Bu	Pn	Hx	Hp	Oc

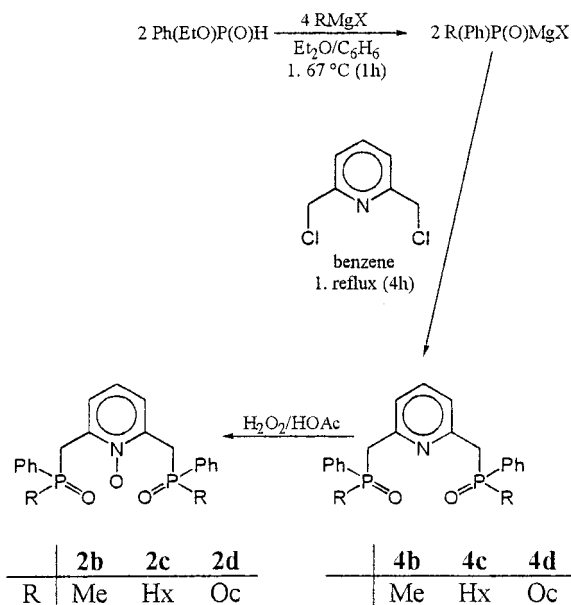
addition are difficult to remove. The other derivatives are most cleanly prepared by use of the phosphino Grignard species R₂P(O)MgBr that are generated by extension of the procedures described by Hays¹⁹ and Gatrone.¹⁷ The yields of the intermediate BMNOPOPO compounds **3c–j** range from 95% to 70%, and each is isolated in a pure state. The subsequent N-oxidations that give the target ligands **1c–j** provide yields of 89–74%. In a related fashion, the asymmetric examples (R ≠ R') are obtained as described in Schemes 3 and 4. The derivative **2a**, containing the Ph(Bz)P(O)– fragments, was prepared by use of an Arbusov reaction, while **2b–d** were obtained through the phosphino Grignard reagents RR'P(O)MgX. The intermediate BMNOPOPO compounds **4a–d** were obtained with yields ranging between 97% and 42% and the BMNOPOPO compounds **2a–d** with yields of 54–94%. The poor yields were encountered with the Ph(Me)P(O)– derivatives **4b** and **2b**. Otherwise, these reactions are efficient and easily performed.

(19) Hays, H. R. *J. Org. Chem.* **1968**, *33*, 3690.

Scheme 3



Scheme 4



The intermediate BMNPOPO compounds **3b–j** and **4a–d** have been characterized by ^1H , ^{13}C , and ^{31}P NMR spectroscopy, and all of these data are summarized in the Supporting Information. The ^{31}P resonances fall in the ranges expected for $\text{R}_2\text{P}(\text{O})\text{CH}_2$ ($\text{R} = \text{R}' = \text{aryl}$ or alkyl) and $\text{RR}'\text{P}(\text{O})\text{CH}_2$ ($\text{R} \neq \text{R}' = \text{Ph}$, alkyl).^{20,21} In addition, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ resonances assigned to the $\text{R}_2\text{P}(\text{O})\text{CH}_2$ and $\text{RR}'\text{P}(\text{O})\text{CH}_2$ substituent groups are diagnostic of these fragments. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are also useful for monitoring the progress of the N-oxidation reactions. The target fully oxidized BMNOPOPO ligands, **1b–j** and **2a–d**, have been characterized²² by FAB mass spectrometry, FTIR,²³ and ^1H , ^{13}C , and ^{31}P NMR spectroscopy.²⁴ Some summary comments are provided. The

FAB-MS spectra uniformly display $(\text{M} + 1^+)$ as the most intense ion while the (M^+) peak is much weaker (3–10%). This is a common observation for BMNOPOPO ligands.^{5,6} The $(\text{M} + 1 - \text{O}^+)$ ion (10–15%) also is a recurrent feature in these spectra. The infrared spectra of **1b–j** and **2a–d** display absorptions in the ranges 1260–1240 and 1170–1150 cm^{-1} that can be assigned to the ν_{NO} and ν_{PO} stretching frequencies, respectively.²³ The $^{31}\text{P}\{^1\text{H}\}$ spectra display a single resonance in the range δ 30–40.²⁴ The $^{13}\text{C}\{^1\text{H}\}$ resonances for the C_1 methyl groups and the C_2 and C_6 ring atoms are shifted downfield of the resonances in the BMNPOPO precursors. The data are consistent with the expected electronic shifts as alkyl groups replace aryl groups in the molecules.

Since the extent of organic solubility of the new ligands is important to future studies of the liquid–liquid extraction properties, the solubilities in CHCl_3 , Et_2O , benzene, toluene, xylene, pentane, hexane, and heptane were determined. All are soluble in CHCl_3 . In the series **1a–j**, the hydrocarbon solubility increases with increasing chain length. In particular, **1f–j** show good solubility in alkanes, which bodes well for successful applications in liquid–liquid extractions.

It is important to determine if the organic substitutions on **1** alter the tridentate coordination characteristic displayed by **1a** toward trivalent lanthanide ions.⁵ Therefore, the coordination chemistry of **1b–j** and **2a–d** toward $\text{Ln}(\text{III})$ ions has been broadly surveyed. Unfortunately, most of the 1:1 and 2:1 L/M mixtures produce oily complexes that are difficult to fully characterize. In general, it is found that the infrared spectra contain bands in the regions 1234–1222 cm^{-1} that are tentatively assigned to ν_{NO} and 1124–1107 cm^{-1} that are assigned to ν_{PO} . All are shifted to lower frequency than the corresponding stretches in the free ligands as would be anticipated with metal ion binding. Of course, the denticity of the ligands cannot be unambiguously assigned from these data. Hence, the molecular structures of three 1:1 complexes, $\text{Yb}(\mathbf{1d})(\text{NO}_3)_3 \cdot \text{Me}_2\text{CO}$, $\text{Er}(\mathbf{2a})(\text{NO}_3)_3$, and $\text{Nd}(\mathbf{2a})(\text{NO}_3)_3$, and a 2:1 complex, $[\text{Nd}(\mathbf{1c})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3 \cdot \text{H}_2\text{O} \cdot 2.5 \text{ MeCN}$, that formed suitable crystals were determined by single-crystal X-ray diffraction analyses.

The early lanthanide complex, $\text{Nd}(\mathbf{2a})(\text{NO}_3)_3$, and the late lanthanide complex, $\text{Er}(\mathbf{2a})(\text{NO}_3)_3$, are isostructural and related to the previously reported structure of the late lanthanide complex, $\text{Yb}(\mathbf{1a})(\text{NO}_3)_3 \cdot \text{MeOH}$.⁵ A view of the Er complex is presented in Figure 1, and bond lengths appear in Table 2. The lanthanide ions have a nine-coordinate inner-sphere environment composed of the three oxygen donor atoms from **2a** as well as six oxygen atoms from three bidentate nitrate groups. The resulting coordination polyhedra approximate a distorted tri-capped trigonal prism. The M–O bond lengths involving the ligand donor atoms are similar within each complex: $\text{Nd}-\text{O}(\text{P})$ 2.390(3) Å, 2.378(3) Å and $\text{Nd}-\text{O}(\text{N})$ 2.382(3) Å; $\text{Er}-\text{O}(\text{P})$ 2.280(7) Å, 2.281(6) Å and $\text{Er}-\text{O}(\text{N})$, 2.278(7) Å. The differences between the complexes are consistent with the larger ionic radius for Nd(III), 1.12 Å, vs Er(III), 1.00 Å.²⁵ These Ln–O distances may be compared against those in the previ-

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(21) Verkade, J. G.; Quin, L. D. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; VCH: Deerfield Beach, FL, 1987.

(22) As noted in our earlier reports,^{5,6} **1** and its pyridine derivatives tend to give CHN analyses that are low in carbon (5–8%) due to incomplete combustion. The same observation has been made with several of the species described in this study. Mass spectra have been used to confirm the identity of the compounds. In addition, most of the compounds are solids that display sharp melting points consistent with high purity.

(23) Phosphonates and phosphine oxides display a strong infrared P=O stretch in the region 1270–1150 cm^{-1} , and phenylphosphine oxide units typically have a P=O stretch at the low end of this range. The ν_{PO} for $[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})]\text{C}_5\text{H}_4\text{N}$ appears at 1185 cm^{-1} . The ν_{NO} for $[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})]\text{C}_5\text{H}_4\text{NO}$ was assigned to a band appearing at 1273 cm^{-1} . By comparison, ν_{NO} in pyridine *N*-oxide appears at 1250 cm^{-1} .⁴

(24) The ^{31}P NMR shifts for organylphosphine oxides usually fall in the range δ 15–50, and the shifts for $[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})]\text{C}_5\text{H}_4\text{N}$ and $[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})]\text{C}_5\text{H}_4\text{NO}$ appear at δ 21.2 and 19.1, respectively.

(25) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1970**, B26, 1076.

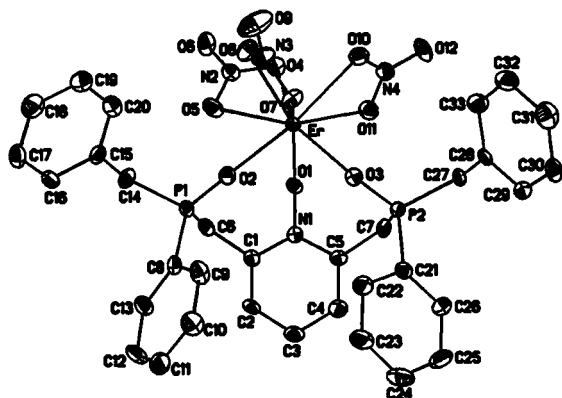


Figure 1. Molecular structure and atom-labeling scheme for Er(**2a**)-(NO_3)₃ (30% thermal ellipsoids).

ously reported complex Yb(**1a**)(NO_3)₃·MeOH. Here the ligand **1a** is more asymmetrically bound: Yb–O(P) 2.252(5) Å, 2.235–(4) Å and Yb–O(N) 2.260(4) Å (Yb(III) ionic radius is 0.98 Å). It is instructive also to compare the sizes of the coordination “footprints” established by the three oxygen donor atoms of **2a** and **1a** in these complexes. It might be expected that the “footprint” triangles would be equilateral; however, they more closely approximate isosceles with the longer edge distance corresponding to the nonbonded P–O···O–P separation involving the pendant phosphine oxide arms: Nd O(1)···O(2) 2.991 Å, O(1)···O(3) 3.040 Å, O(2)···O(3) 3.389 Å; Er O(1)···O(2) 2.900 Å, O(1)···O(3) 2.961 Å, O(2)···O(3) 3.239 Å. These values may be compared against those found in Yb(**1a**)(NO_3)₃·MeOH:⁵ O(1)···O(2) 2.856 Å, O(1)···O(3) 2.871 Å, O(2)···O(3) 3.113 Å. Clearly, the sizes of the “footprints” in the three complexes described so far vary with the charge:radius ratio of the central metal ion. The smallest triangle is formed by the smallest, most polarizing cation, Yb(III). The internal O–O–O angles in the footprint triangles vary slightly as a function of central atom, with the largest variation occurring in the O(2)–O(1)–O(3) angles.²⁶ Last, we note that the three nitrate ions are asymmetrically bonded to the Er ions while only two are asymmetric in the Nd complex.

The structural data for the three 1:1 complexes described above do not reveal a significant impact due to the change in the R groups in the tridentate ligands (**1a**, R = Ph; **2a**, R = Bz). However, a more significant decrease in R group size in **1d** (R = Et) results in interesting structural changes in a fourth complex, Yb(**1d**)(NO_3)₃·Me₂CO. A view of this molecule is shown in Figure 2, and bond lengths and angles are summarized in Table 2. The Yb in Yb(**1d**)(NO_3)₃·Me₂CO is bonded to three oxygen atoms from the tridentate ligand **1d** and six oxygen atoms from three bidentate nitrate anions. In this complex, the resulting nine-vertex inner-sphere coordination polyhedron is best described as a monocapped square antiprism. There is also one molecule of acetone present in the outer sphere. The M–O bond lengths, Yb–O(P) 2.223(3) Å, 2.233(3) Å, and Yb–O(N) 2.278(3) Å, are comparable with those in Yb(**1a**)(NO_3)₃·MeOH;⁵ however, the “footprint” triangle is considerably enlarged with an increased O(2)···O(3) distance and O(2)–O(1)–O(3) angle: O(1)···O(2) 2.958 Å, O(1)···O(3) 2.989 Å, O(2)···O(3) 4.252 Å; angles at O(1) 91.3°, O(2) 44.7°, O(3) 44.1°. This suggests that the sterically large phenyl and benzyl groups in Nd(**2a**)(NO_3)₃, Er(**2a**)(NO_3)₃, and Yb(**1a**)(NO_3)₃·MeOH par-

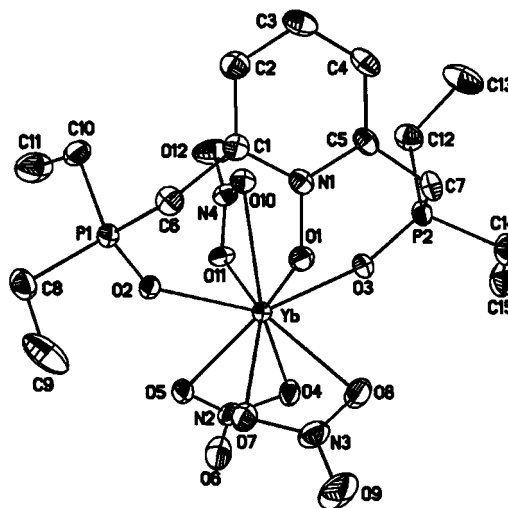


Figure 2. Molecular structure and atom-labeling scheme for Yb(**1d**)-(NO_3)₃·Me₂CO (30% thermal ellipsoids).

ticipate in forming a more compact chelate triangle while the smaller ethyl substituents on the phosphoryl groups in Yb(**1d**)-(NO_3)₃·Me₂CO allow these donor groups to splay out to a greater extent.

An alternative view of the Yb(III) complexes can be derived by considering the metals to be in a six-coordinate pseudooctahedral trigonal antiprismatic geometry formed by the three donor oxygen atoms of **1a** or **1d** and the N atoms of the three inner-sphere nitrate ions. In Yb(**1d**)(NO_3)₃·MeOH the trigonal antiprismatic geometry constructed from O(1), O(2), O(3) and N(2), N(3), N(4) is only moderately distorted from regular.²⁷ The antiprism defined by the same atoms in Yb(**1d**)(NO_3)₃·Me₂CO is highly distorted, and a more regular polyhedron is obtained with O(1), O(3), N(3) and O(2), N(1), N(2) serving as the vertices.

The molecular structure of [Nd(**1c**)₂(H₂O)₂](NO_3)₃·H₂O·(CH₃CN)_{2.5} is shown in Figure 3, and selected bond lengths are summarized in Table 2. The central Nd(III) ion is bonded to six oxygen atoms from two tridentate ligands **1c** and two oxygen atoms from two water molecules. The resulting eight-vertex coordination polyhedron approximates a dodecahedron. The three nitrate ions, a water, and 2.5 CH₃CN reside in the outer coordination sphere. This structure differs from that found for [Yb(**1a**)₂(NO_3)](NO_3)₂·(H₂O)₂·(CH₃CN)_{2.5} wherein a bidentate inner-sphere nitrate ion is found coordinated to the Yb(III) ion instead of two water molecules.⁵ In fact, the [Nd(**1c**)₂(H₂O)₂]³⁺ complex represents the first example where **1** completely displaces all of the nitrate ions from the inner sphere of the lanthanide ion. Although such behavior is common for neutral macrocyclic ligands, the removal of inner-sphere nitrate ions from the lanthanides by acyclic ligands remains relatively uncommon. Three of the Nd–O(P) bond lengths in [Nd(**1c**)₂(H₂O)₂](NO_3)₃·H₂O·(CH₃CN)_{2.5} are identical (av 2.386 Å) and comparable with that described above for Nd(**2a**)(NO_3)₃; however, the fourth Nd–O(P) distance is noticeably shorter, 2.341(6) Å. This probably results from optimization of the ligand arrangements in the inner sphere. The two Nd–O(N) distances

(26) The internal O–O–O bond angles in the footprint triangles at the indicated oxygen atoms are as follows: Nd(**2a**)(NO_3)₃ O(1) 68.4°, O(2) 56.5°, O(3) 55.1°; Er(**2a**)(NO_3)₃ O(1) 67.1°, O(2) 57.4°, O(3) 55.6°; Yb(**1a**)(NO_3)₃·MeOH O(1) 65.8°, O(2) 57.3°, O(3) 56.9°.

(27) The antiprism edge distances for Yb(**1d**)(NO_3)₃·Me₂CO are O(1)···N(2) 3.94 Å, O(1)···N(3) 3.64 Å, O(2)···N(2) 3.37 Å, O(2)···N(4) 3.92 Å, O(3)···N(3) 4.00 Å, and O(3)···N(4) 3.17 Å. The average distance between planes is 2.93(37) Å. The edge distances for Yb(**1a**)(NO_3)₃·MeOH are O(1)···O(2) 2.96 Å, O(1)···N(4) 4.03 Å, O(3)···N(4) 3.10 Å, O(3)···N(2) 4.01 Å, N(3)···N(2) 3.84 Å, and N(3)···O(2) 3.98 Å. The average distance between planes is 2.82(11) Å.

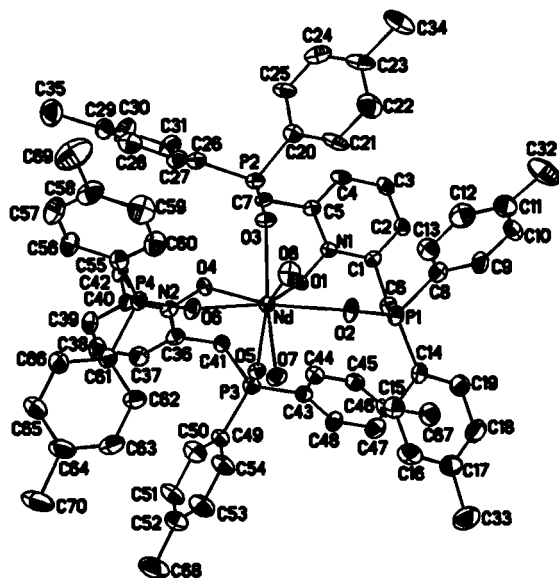


Figure 3. Molecular structure and atom-labeling scheme for $[\text{Nd}(\mathbf{1c})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3 \cdot \text{H}_2\text{O} \cdot 2.5\text{CH}_3\text{CN}$ (25% thermal ellipsoids).

in $[\text{Nd}(\mathbf{1c})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3 \cdot \text{H}_2\text{O} \cdot (\text{CH}_3\text{CN})_{2.5}$ are identical (av 2.506(6) Å); however, they are much longer than the Nd–O(N) distance in $\text{Nd}(\mathbf{2a})(\text{NO}_3)_3$, 2.382 Å. A similar effect is found when comparing Yb–O(N) distances in $[\text{Yb}(\mathbf{1a})(\text{NO}_3)_3] \cdot \text{MeOH}$ (2.260(4) Å)⁵ and in $[\text{Yb}(\mathbf{1a})_2(\text{NO}_3)](\text{NO}_3)_2(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_{2.5}$ (av 2.375 Å).⁵ The triangular coordination footprints for the ligand **1c** on Nd(III) in the 1:1 and 2:1²⁸ complexes also reflect this effect since the longer Nd–O(N) distances stand the ligand

off from the central atom, leading to a more open nonbonded edge distance between the phosphoryl oxygen atoms. We anticipate that this geometrical result should reveal itself in calorimetric ligand binding analyses which we hope to undertake soon.

Conclusion

The new derivatives of the tridentate ligand **1** described in this study show greatly enhanced organic solvent solubility compared to **1a**, and this will permit thorough studies of the liquid–liquid extraction performance of **1** toward lanthanide and actinide ions. It is anticipated that one or more of the derivatives will show dramatically improved extraction ability compared to the commonly employed CMPO ligands. In addition, the new ligands will allow us to begin parallel thermodynamic ligand binding studies. The quantitative results will help direct us in further ligand design efforts for f-element ions.

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Supporting Information Available: ¹H and ¹³C NMR data and four crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(28) The nonbonded O···O contact distances in $[\text{Nd}(\mathbf{1c})_2(\text{H}_2\text{O})_2]^{3+}$ are O(1)···O(2) 2.896 Å, O(1)···O(3) 3.002 Å, O(2)···O(3) 3.529 Å, O(4)···O(5) 2.922 Å, O(4)···O(6) 2.891 Å, and O(5)···O(6) 3.535 Å.