Synthesis and Coordination Chemistry of 1,3-Bis(diphenylphosphinomethyl)benzene *P,P'*-Dioxide

Yun-Chou Tan, Xin-Min Gan, Jesse L. Stanchfield, Eileen N. Duesler, and R. T. Paine*

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

Introduction

Recent studies of the coordination chemistry of 2,6-bis-(diphenylphosphinomethyl)pyridine *N,P,P'*-trioxide (**1**) (R = Ph; R′ = H) have revealed that this ligand acts as a tridentate chelator toward a number of trivalent and tetravalent cations.[1−3] Furthermore, companion liquid−liquid extraction studies with **1** indicate that it is an excellent reagent for removing trivalent lanthanide and actinide ions from concentrated nitric acid and hydrochloric acid nuclear process waste solutions.[3−5] In an effort to understand how this ligand functions as a powerful extractant, we have been studying the impacts on chelation behavior affected by structural and electronic modifications on **1**. These include substituent group modifications on the phosphoryl groups (R) and on the methyl carbon atoms (R′).[6−9] These modifications influence chelation in only modest ways except for cases where R′ imposes large steric restrictions on the orientational flexibility of the methylphosphine oxide "arms".[6]
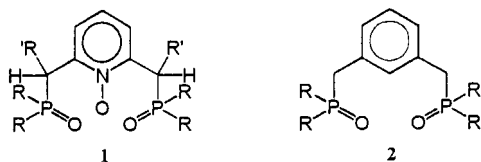
During the course of our work on modifications of **1**, we became interested in the bifunctional ligand 1,3-bis(diphenylphosphinomethyl)benzene (**2**) (R = Ph), a close relative of **1** with the active donor *N*-oxide group removed and replaced by a coordination silent arene CH group. This ligand has been briefly described in Russian literature,[10] and extraction data for

trivalent actinide ions in HNO₃ solutions[11] suggest that **2** is a much weaker extractant than **1**. In order to examine the behavior of **2** in greater molecular level detail, we have improved the synthesis and studied its coordination chemistry toward trivalent ions Y(III) and Er(III). These results are compared against the chemistry of **1**.

Experimental Section

General Information. The organic reagents used for the syntheses were purchased from Aldrich Chemical Co. and used without purification unless noted otherwise. The inorganic reagents were purchased from Fisher Scientific, and the Er(NO₃)₃·nH₂O and Y(NO₃)₃·nH₂O were obtained from Ventron. Infrared spectra were recorded on a Mattson 2020 FTIR spectrometer, and mass spectra were obtained from the Midwest Center for Mass Spectometry, at the University of Nebraska. NMR spectra were measured on Bruker FX-250 and JEOL GSX-400 spectrometers. The NMR standards were Me₄Si (^{1}H, ^{13}C) and 85% H₃PO₄ (^{31}P), and downfield shifts were assigned as +δ. Elemental analyses were obtained from Galbraith Laboratories.

Synthesis of 1,3-Bis(diphenylphosphinomethyl)benzene *P,P'*-Dioxide (2). Excess thionyl chloride (80 mL) was added to a 250 mL three-necked round bottom flask equipped with a reflux condenser, a solids addition tube, a dry nitrogen inlet, and a stir bar. The flask was purged with a slow stream of dry nitrogen and cooled with an ice bath. The 1,3-benzenedimethanol (10.0 g, 0.0724 mol) was added in small portions from the solids addition tube (1 h) to the stirred SOCl₂ and the mixture subsequently refluxed (4 h). The excess thionyl chloride was removed by vacuum evaporation, and the remaining light brown residue was treated with heptane (100 mL). The clear, light orange solution containing the product was decanted from a small amount of sludge and cooled (−20 °C). White crystals of 1,3-bis(chloromethyl)-benzene (**3**) deposited overnight and were recovered by filtration and dried: yield 9.31 g (73.8%). NMR spectra (23 °C, CDCl₃): ^{1}H δ 4.57 (CH₂, 4H), 7.33 (m, 3H), 7.41 (1H); ^{13}C {^{1}H} δ 45.71 (CH₂), 128.46, 128.58, 129.06, 137.93. Two approaches were used to obtain the bisphosphine oxide.

Method A. A sample of **3** (4.0 g, 0.023 mol) was dissolved in triglyme (20 mL) and added to a three-necked round bottom flask fitted with a condenser, a nitrogen gas inlet, and an addition funnel. The top of the condenser was connected to a vacuum line. The nitrogen inlet and vacuum outlet valves were adjusted to maintain a pressure of 20 mTorr. A solution containing Ph₂POEt (11.1 g, 0.0482 mol) in triglyme (5 mL) was added to the dropping funnel. The solution containing the 1,3-bis(chloromethyl)benzene was heated to 150 °C, and the solution of Ph₂POEt was added dropwise. The resulting mixture was heated for an additional period (3 h) at 20 mTorr, and then the triglyme was removed at 80−100 °C (10⁻³ Torr). A light yellow solid remained, which was recrystallized from ethyl acetate, leaving a colorless crystalline solid, **2**: yield 10.2 g, 87.6%; mp 77−79 °C.

Method B. Phenylmagnesium bromide (12.7 mL, 3.0 M solution in ether, 38 mmol) was added dropwise, under dry nitrogen purge, to a solution of ethyl phenylphosphinate (3.2 g, 19 mmol) in ether (10 mL) and dry benzene (10 mL). The temperature of the mixture rose during addition; when addition was complete, the mixture was heated (1 h) with an oil bath (68 °C). The resulting Ph₂P(O)MgBr solution was added, without isolation, to 1,3-bis(chloromethylbenzene) (1.5 g, 8.6 mmol) in tetrahydrofuran (THF) (10 mL), and the mixture was refluxed (4 h). The mixture was then cooled, and most of the solvent was swept from the reaction vessel by exposing it to a purge of dry nitrogen at 25 °C. The remaining sticky oil was treated with saturated aqueous NH₄Cl (25 mL) and CHCl₃ (30 mL) and the mixture transferred to a separatory funnel. The organic and aqueous (pH = 7−8) phases were separated, and the aqueous phase was extracted with CHCl₃ (3 × 20

* To whom correspondence should be addressed. Phone: (505) 277-1661. E-mail: rtpaine@unm.edu.
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Table 1. Crystallographic Data

	2·H$_2$O	[Er(**2**)(NO$_3$)$_2$](NO$_3$)· $^1/_2$MeOH	[Y(**2**)(NO$_3$)$_2$](NO$_3$)· MeOH
empirical formula	C$_{32}$H$_{30}$O$_3$P$_2$	C$_{64.5}$H$_{58}$ErN$_3$O$_{13.5}$P$_4$	C$_{65}$H$_{60}$N$_3$O$_{14}$P$_4$Y
fw	524.50	1382.28	1319.95
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	10.082(2)	10.507(2)	10.525(3)
b, Å	10.185(3)	13.098(3)	13.132(3)
c, Å	26.724(8)	25.151(5)	25.184(5)
α, deg	90	78.85(2)	78.99(2)
β, deg	92.72(2)	87.33(1)	87.15(2)
γ, deg	90	75.59(2)	75.48(2)
vol, Å^3	2741(1)	3289(1)	3307(1)
Z	4	2	2
density, g cm^{-3}	1.271	1.396	1.325
μ, mm^{-1}	0.190	1.436	1.042
θ range, deg	2.13–23.50	1.96–25.04	1.96–25.00
no. of reflns collected	8409	23138	22925
no. of indep reflns	4066	11574	11600
R1^a [$I > 2\sigma(I)$]	0.0368	0.0548	0.0650
wR2^b	0.0850	0.1232	0.1514

^{a} R1 = $\sum||F_o| - |F_c||/\sum[F_o]$. ^{b} wR2 = $[\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

mL). The combined CHCl$_3$ phases were dried (Na$_2$SO$_4$), the CHCl$_3$ was vacuum evaporated, the residue was dissolved in ethyl acetate (10 mL), and the solution was cooled overnight in the refrigerator. The white precipitate **2** was collected by filtration and washed with fresh cold ethyl acetate: yield 3.80 g (87.3%); mp 77–79 °C. Anal. Calcd for **2**·H$_2$O, C$_{32}$H$_{30}$O$_3$P$_2$: C, 73.28; H, 5.77. Found: C, 73.02; H, 5.77. Infrared spectrum (KBr, cm^{-1}): 1190 (s, ν_{PO}), 1163 (m). Mass spectrum (HREI): calcd for ^{12}C$_{32}$H$_{28}$O$_2$P$_2$, 506.156457; found, 506.156690 (−0.5 ppm). NMR spectra (23 °C, CDCl$_3$): ^{31}P{^{1}H} δ 30.0; ^{1}H δ 3.49 (d, J_{PH} = 13.8 Hz, 4H, H$_1$), 6.88–6.96 (m, 4H), 7.34–7.43 (m, 12H), 7.55–7.64 (m, 8H); ^{13}C{^{1}H} δ 37.74 (d, J_{PC} = 66.5 Hz, C$_1$), 128.34 (d, J_{PC} = 11.9 Hz, C$_8$), 128.35 (C$_4$), 130.94 (C$_3$), 130.95 (d, J_{PC} = 9.4 Hz, C$_7$), 131.19 (d, J_{PC} = 10.2 Hz, C$_2$), 131.60 (C$_9$), 131.98 (d of d, J_{PC} = 5.5 Hz, C$_5$), 132.15 (d, J_{PC} = 99.1 Hz, C$_6$).

Synthesis of the Complexes. Lanthanide nitrate salts (0.2 mmol) and ligand (0.6 mmol) were combined in MeOH (10 mL) and briefly stirred. Ethyl acetate (5 mL) was added, and the mixture was filtered. The filtrate was placed in a loosely capped vial, and slow solvent evaporation produced pink (Er) and colorless (Y) crystalline complexes. Infrared spectrum (KBr, cm^{-1}): Er(**2**)$_2$(NO$_3$)$_3$ 1095 (s) (ν_{PO}); Y(**2**)$_2$-(NO$_3$)$_3$ 1095 (s) (ν_{PO}). Anal. Calcd for Er(**2**)$_2$(NO$_3$)$_3$·$^1/_2$MeOH, C$_{64.5}$H$_{58}$N$_3$O$_{13.5}$P$_4$Er: C, 56.04; H, 4.23; N, 3.04. Found: C, 55.93; H, 4.28; N, 3.06. Calcd for Y(**2**)(NO$_3$)$_3$·MeOH: C$_{65}$H$_{60}$N$_3$O$_{14}$P$_4$Y: C, 59.14; H, 4.58; N, 3.18. Found: C, 59.25; H, 4.57; N, 3.21.

X-ray Diffraction Studies. The data crystal for **2**·H$_2$O was obtained by slow evaporation (1 week) of a filtered solution of **2** (200 mg) in CH$_2$Cl$_2$ (5 mL) and EtOAc (10 mL). Suitable single crystals of the coordination complexes were obtained from the preparative workups. Crystals for the ligand and each complex were mounted in glass capillaries, and X-ray data were collected by variable-speed ω scans on a Siemens R3m/V diffractometer equipped with a graphite monochromator using Mo Kα radiation (λ = 0.71073 Å). Lattice and data collection parameters are summarized in Table 1. All calculations were performed with SHELXTL.[12] The structure of the ligand was solved by direct methods, and the structures of the complexes were solved by standard Patterson interpretations and difference Fourier methods. Full matrix least-squares refinements were employed. Data were corrected for absorption using semiempirical ψ-scans. The Er complex showed an approximate 11% decrease in scattered intensities of the standards during data collection, and the Y complex showed an 8% decrease. This may result from partial loss of MeOH from the respective lattices. All inner sphere heavy atoms were refined anisotropically. The unbound outer sphere nitrate ion in each structure was disordered with the

(12) Sheldrick, G. M. *Nicolet SHELXTL Operations Manual;* Nicolet XRD Corp.: Cupertino, CA, 1981. The least-squares refinement minimizes $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F)^2 + gF^2]$.

following occupancies: Er 0.612 and 0.388; Y 0.667 and 0.333. The outer sphere MeOH is also disordered with the following occupancies: Er, 0.5 molecule/Er, 0.281 and 0.219; Y, 1 molecule/Y, 0.5 and 0.5.

Results and Discussion

In 1979, Kabachnik[10] reported the synthesis of 1,3-bis-(diphenylphosphinomethyl)benzene *P,P′*-dioxide **2** from an Arbusov reaction between Ph$_2$POEt and 1,3-bis(bromomethyl)-benzene in hot (140 °C) xylene. The compound was recrystallized from ethanol, and elemental analyses were consistent with the composition C$_{32}$H$_{28}$O$_2$P$_2$. The reported yield was 68%, and no other characterization data, except for a melting point (133–135 °C), were provided. We have been interested in comparing the coordination and extraction behaviors of derivatives of **1** and **2**; hence the synthesis of **2** (R = Ph) was reexamined. A related Arbusov reaction (method A) between Ph$_2$POEt and 1,3-bis(chloromethyl)benzene in triglyme (eq 1) gives a white crystalline solid in 87% yield, with a significantly lower melting point (77–79 °C). In addition, the carbon analysis is low compared to the expected formula. This led us to explore an alternative route to **2** through addition of the phosphino Grignard reagent Ph$_2$P(O)MgCl to 1,3-bis(chloromethyl)benzene (method B). This route provides a white crystalline solid, in 87% yield, with a melting point and CH analysis identical with those of samples obtained from method A. A high-resolution electron impact mass spectrum contains a parent ion envelope with the most intense ion at m/e = 506.15669 (calcd for ^{12}C$_{32}$H$_{28}$O$_2$P$_2$: 506.15646) consistent with the formula proposed by Kabachnik.[10] The infrared spectrum of **2** shows a strong band at 1190 cm^{-1} diagnostic of the P=O stretching frequency. The ^{31}P NMR spectrum displays a single resonance, δ 30.0, that is comparable to the shift reported for **1**, δ 31.4.[1,2] The ^{31}C{^{1}H} NMR spectrum for **2** contains a high-field doublet, δ 37.74, J_{PC} = 66.5 Hz, that is assigned to the carbon atoms (C$_1$, C$_{1'}$). In addition, eight arene resonances, δ 128–133, are resolved for the eight inequivalent carbon atoms, C$_2$–C$_5$, C$_6$–C$_9$. These data are similar to those obtained from **1**: δ 31.5 (J_{PC} = 67.0 Hz) and δ 124–133. The ^{1}H NMR spectrum of **2** shows a doublet at δ 3.49, J_{PH} = 13.8 Hz, that is assigned to C$_1$H$_2$, C$_{1'}$H$_2$, and a similar resonance is seen in **1**: δ 4.12, J_{PH} = 6.9 Hz.


(1)
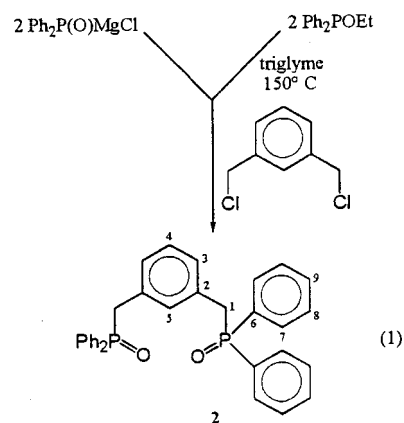
The characterization data for **2** prepared by methods A and B are consistent with the structure proposed by Kabachnik except that our elemental analyses and melting point data are at odds with the earlier report. As a result, the molecular structure of **2** was examined by single-crystal X-ray diffraction techniques. A view of the molecule is shown in Figure 1, and pertinent bond lengths are listed in Table 2. On the basis of the structure determination, the origin of the discrepancies in melting

Table 2. Selected Bond Distances (Å)

	2·H₂O		[Er(**2**)(NO₃)₂](NO₃)·¹/₂MeOH		[Y(**2**)(NO₃)₂](NO₃)·MeOH	
M−O(P)			Er−O(1)	2.243(5)	Y−O(1)	2.257(5)
			Er−O(2)	2.252(5)	Y−O(2)	2.266(5)
			Er−O(3)	2.249(5)	Y−O(3)	2.261(5)
			Er−O(4)	2.233(5)	Y−O(4)	2.248(5)
M−O(N) nitrate			Er−O(6)	2.445(6)	Y−O(6)	2.465(6)
			Er−O(7)	2.461(6)	Y−O(7)	2.484(6)
			Er−O(9)	2.473(6)	Y−O(9)	2.482(6)
			Er−O(10)	2.455(6)	Y−O(10)	2.475(6)
P=O	P(1)−O(1)	1.482(2)	P(1)−O(1)	1.504(5)	P(1)−O(1)	1.501(5)
	P(2)−O(2)	1.488(2)	P(2)−O(2)	1.517(5)	P(2)−O(2)	1.504(5)
			P(3)−O(3)	1.506(5)	P(3)−O(3)	1.493(5)
			P(4)−O(4)	1.505(5)	P(4)−O(4)	1.506(5)
P−C	P(1)−C(7)	1.811(2)				
	P(2)−C(8)	1.810(2)				
C−C	C(6)−C(8)	1.504(3)				
	C(2)−C(7)	1.509(3)				
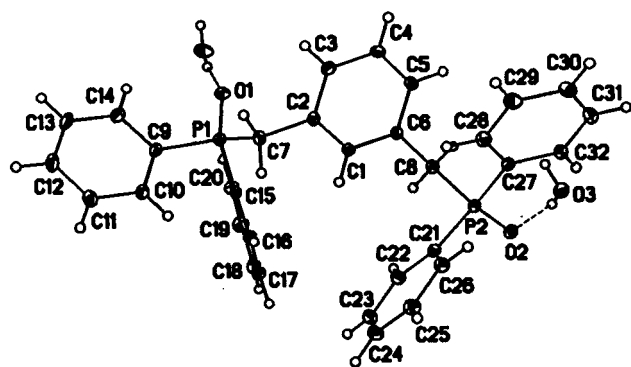
Figure 1. Molecular structure and atom-labeling scheme for [Ph₂P-(O)CH₂]₂C₆H₄·H₂O.

points and CH analyses becomes clear. The structure contains one molecule of water per molecule of **2**, and the resulting composition, **2**·H₂O, C₃₂H₃₀O₃P₂, is in close agreement with the observed CH analytical data. Further, it might be expected that the melting point of an aquo complex, **2**·H₂O, would be lower than that obtained from anhydrous **2**. The origin of the water in the crystals likely is from the reaction mixture workup or the ethyl acetate used to recrystallize **2**. It is interesting that the hydrogen-bonded complex **2**·H₂O does not involve chelation of one water molecule by the two Ph₂P(O) donor groups in **2**. Instead, the Ph₂P(O) groups in **2** are rotated away from each other in an anti-like configuration, and the water molecule bridge bonds between two ligand units. The water is placed relatively symmetrically between the P=O groups of the two ligands: O(1)−H(3a) 2.00(3) Å, O(2)−H(3b) 2.13(3) Å, O(1)···O(3) 2.856(3) Å, O(2)···O(3) 2.869(3) Å. The two terminal P=O distances are equivalent within 3σ of the esd's, and the average distance, 1.485(2) Å, is identical to the value in **1**, 1.480(3) Å.[2] Hence, at the level of accuracy of this data set, the H-bonding interactions do not result in P=O bond lengthening as found in metal ion complexes of phosphoryl ligands. The average P−C(methyl) distance, 1.810(2) Å, and C(methyl)−C(aryl) distance, 1.506(3) Å, are comparable with the related distances in **1**: 1.813(4) and 1.495(5) Å, respectively.

The groups of Kabachnik and Myasoedov have previously reported solvent extraction data for a number of closely related polyphosphine oxide ligands acting on aqueous nitric acid solutions containing hexavalent uranyl, tetravalent Pu, and trivalent lanthanide (Eu) and actinide (Cf, Bk, Cm, and Am) f-element cations.[10,11,13−15] In most cases, ([ligand] = 0.025 M, CHCl₃ solution) the absolute values of the distribution ratio, D = [metal]ₒᵣg/[metal]ₐq, are small (<1). However, the values

tend to increase with increasing aqueous acid concentration, and some binary element selectivities are large.[15] These responses make these ligands of some practical importance, and it is of interest to determine what factors influence the extraction behaviors toward particular ions. Pertinent to the present study, the extraction performance of **2** relative to the ortho-substituted analogue, 1,2-bis(diphenylphosphinomethyl)benzene *P,P'*-dioxide **4**, has been explored.[10,11,13−15] Molecular mechanics calculations were used to suggest that the conformational energetics of **4** favor coordination with UO₂²⁺ and Pu(IV) while **2** prefers coordination with trivalent cations with slight selectivity for Eu(III) over Am(III). Implicit in these discussions was the assumption that bidentate chelate structures were adopted by both ligands. However, as far as we are aware, confirmation of this coordination mode with f-element ions has not been demonstrated in solution or solid states. Indeed, the coordination chemistry of **2** has only been scarcely examined toward Co(II), Cu(I), and Cu(II),[16] and the molecular structures were not determined. Further, the anti conformation of **2** described here suggests the possibility that the ligand might adopt bridged structures.

In the present study, we prepared and isolated coordination complexes of **2** with several Ln(NO₃)₃ salts. In all cases, 2:1 ligand/metal complexes are isolated even when excess ligand is provided to the metal. Two complexes, Y(**2**)₂(NO₃)₃ and Er-(**2**)₂(NO₃)₃, form single crystals from MeOH solution, and they have been isolated and structurally characterized by X-ray diffraction techniques. The structures contain a central metal ion (Er or Y) chelated by two bidentate ligands **2** and two bidentate nitrate ions. The third nitrate is found disordered in the outer coordination sphere along with MeOH solvate (Er, ¹/₂MeOH; Y, MeOH). A view of the Er(III) complex is provided in Figure 2. The average M−O(P) bond lengths are Er−O(P) 2.244(5) Å (range 2.233(5)−2.252(5) Å) and Y−O(P) 2.258-(5) Å (range 2.248(5)−2.266(5) Å). The slightly longer average value for the Y(III) complex is expected given the larger ionic radius of Y: Er(III) (CN = 8), 1.00 Å, and Y(III) (CN = 8), 1.02 Å.[17] The O···O nonbonded ligand bite distances on the

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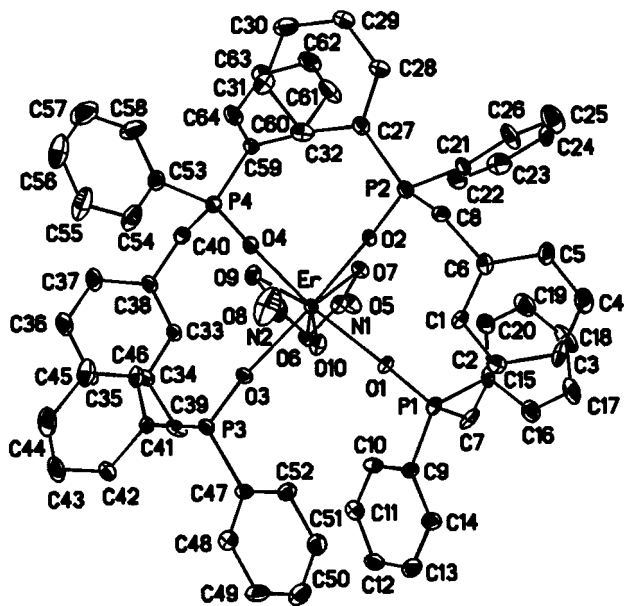(17) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1970**, *B26*, 1076.

Figure 2. Molecular structure and atom-labeling scheme for [Er(**2**)₂-(NO₃)₂](NO₃)·¹/₂MeOH.

Y(III) ion, 3.198 and 3.266 Å, also are slightly longer than those on the smaller Er(III) ion. The inner sphere nitrate ions are planar, and the planes are oriented approximately perpendicular to each other. They are symmetrically chelated at a 3σ esd level of comparison, and the average M−O(N) bond lengths are Er−O(N), 2.458 Å, and Y−O(N), 2.476 Å. Once more, the difference in the average values compares favorably with the difference in metal ionic radii. The average P=O bond lengths, (Er)O=P, 1.508(5) Å, and (Y)O=P, 1.501(5) Å, are slightly elongated compared to the average P=O distance in the free ligand, 1.485(2) Å. The bond lengthening and the short M−O(P) distances in the complexes are consistent with the coordination shifts, $\Delta\nu_{PO} = 95$ cm⁻¹, found from the IR spectral data.[18] By

comparison, Bond[19] has observed that CHCl₃ solutions of **2** exposed to strongly acidic aqueous solutions (2−6 M HNO₃) show large $\Delta\nu_{PO}$ shifts of 90−110 cm⁻¹. More weakly acidic solutions (0.1−1 M HNO₃) display little or no coordination shift.

The structural results confirm that the methylphosphine oxide coordination arms in **2** are relatively free to reorient from the anti-like orientation in the free ligand to the syn-like orientation in its chelate complexes. In addition, it is apparent that the tridentate ligand **1** and the bidentate ligand **2** adopt nearly superimposable ligand backbone geometries in their respective bis(ligand) M(III) complexes. In the latter complexes, although there is no coordinative interaction, the C(1)−H(1) and C(33)−H(33) bond vectors point toward the central Er(III). These vectors occupy the same steric space as the strongly coordinating *N*-oxide donor interactions in the Ln(**1**)₂³⁺ complexes. The similar ligand geometries in these two classes of complexes are consistent with the assumption that there is minimal or at least comparable ligand strain energy expended in adopting the bidentate and tridentate structures. As a result, the addition of the strongly donating N−O groups in the complexes of **1** would be expected to make its complexes significantly more stable. The complexes of **2** appear to make up for part of this reduction in complexation energy by including another inner sphere bidentate nitrate group. However, available extraction data[4,10,13] clearly show that **1** forms much more stable complexes.

Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The ligand **2** also displays a medium-intensity band at 1163 cm⁻¹, but it is not strongly affected by metal coordination.

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