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Synthesis and lanthanide coordination chemistry of 2-[(phosphinoyl)methyl]-4,5-dihydrooxazole and 2-[(phosphinoyl)methyl]benzoxazole ligands

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1. Introduction

The synthesis and reactivity of organic molecules containing 2oxazoline (A) and 2-benzoxazole (B) ring fragments have been actively studied due, in part, to their appearance in natural systems and their use as platforms for the construction of hybrid, hemilabile ligands. In the latter case, **A** and **B** have been decorated with, for example, hydroxyphenyl [1-3], pyridine [3-11], quinolinyl [12,13], thiol [14], phosphine [15-25] and phosphine oxide [26-29] donor groups. The coordination chemistry of the ligands has been elaborated largely by using late, soft, d-block metal ions in efforts to obtain asymmetric catalysts for various organic transformations. Portions of that coordination chemistry for the oxazoline-based ligands have been thoroughly reviewed [30,31]. In all cases where molecular structures have been determined by crystallographic methods, the hybrid ligands have been observed to chelate to metal cations by using the oxazoline or benzoxazole ring N_{oxaz} -atom and one or two *exo*-donor atom(s). The O_{oxaz} -atom has not been found to participate in the coordination chemistry. This observation is consistent with photoelectron spectroscopic analyses and quantum mechanical computations that indicate that the Noxaz-atom lone pair lies at lower energy than the Ooxaz-atom lone pair [32].



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ABSTRACT

Syntheses for [(diphenylphosphinoyl)methyl]-4,5-dihydrooxazole (**2**) and [(diarylphosphinoyl)methyl] benzoxazoles [aryl = phenyl (**3**), tolyl (**4**), 2-trifluoromethylphenyl (**5**) and 3,5-bis(trifluoromethyl)phenyl (**6**)] have been developed. Each ligand has been characterized by spectroscopic methods and single crystal X-ray diffraction analyses have been completed for **2**, **3**, **4** and **5**. The coordination chemistry of the ligands with Nd(NO₃)₃ and Yb(NO₃)₃ has been examined and structure determinations for [Nd(**2**)₂ (NO₃)₃(CH₃OH)], [Nd(**2**)₂(NO₃)₃], [Yb(**3**)₂(NO₃)₃(H₂O)]·0.5(CH₃OH), [Nd(**3**)₂(NO₃)₃]·3(CHCl₃), [Nd(**4**)₂ (NO₃)₃(H₂O)] and [Yb(**5**)₂(NO₃)₃(H₂O)]·0.5(CH₃CN) are reported. Depending upon conditions, the ligands act as monodentate PO or bidentate, chelating PO,N donors.

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Despite the expansive options available for functionalization of A and **B**, relatively few reports of attempts to prepare ligands that effectively bind with f-block metal ions have appeared [5,6,9,11,33-37]. In our group, we have been engaged in ligand design efforts for lanthanide and actinide ions, and that work has led to development of bifunctional ligand classes **C–E** [38–51]. In each case, the hybrid PO,CO and PO,NO ligands were expected to form bidentate chelate complexes with hard metal cations by using both available O-atom donor centers, and it was anticipated that the phosphoryl oxygen atom would provide the stronger interaction. Indeed, in all structurally characterized examples except one, C-E were found to form bidentate chelates [38–48]. In the exception, $[Er(C)_2(NO_3)_3(H_2O)]$, both C (R = iPr, R' = Et) ligands were observed to bind with Er(III) through monodentate PO interactions while the amide carbonyl groups interacted, via hydrogen bonds, with an inner sphere water molecule [39]. These results led us to examine related N,CO and NO,CO hybrid ligand architectures including those of type F-H [49-51]. Ligands G and H were observed to form bidentate complexes although a derivative of **G** with a hydroxyl group on the methylene carbon atom was found to chelate through the amide carbonyl O-atom and the hydroxyl O-atom [50]. In contrast, spectroscopic data suggested that examples of F behaved only as monodentate CO donor ligands with the pyridine N-atom hydrogen bonded to inner sphere solvent (H₂O or MeOH). Unfortunately, efforts to confirm this bonding mode by crystallographic analyses have, so far, been unsuccessful. Nonetheless, these findings suggested the possibility that new ligands of types I and J, containing a very hard PO donor center and a softer N_{ring} donor site, might produce complexes with both monodentate and bidentate coordination modes. Herein, we report the syntheses of methylphosphoryl decorated derivatives of I (R = Ph) and I (R = Ph, Tol,



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 $(CF_3)C_6H_4$ and $(CF_3)_2C_6H_3$) and structurally characterized coordination compounds of each ligand that show evidence for hemilabile interactions on lanthanide cations.



2. Experimental

2.1. Materials and characterization

Organic solvents were purchased from VWR and synthetic reagents were obtained from Aldrich Chemical Co. Infrared spectra were recorded on a Bruker Tensor 27 benchtop spectrometer and NMR spectra were measured with Bruker FX-250 and Avance 300 and 500 spectrometers using Me₄Si (¹H, ¹³C) and 85% H₃PO₄ (³¹P) as external standards. Downfield shifts were given + δ values. Mass spectra were obtained from the UNM Mass Spectrometry Center. Elemental analyses were obtained from Galbraith Laboratories. The preparations of N-(2-hydroxyphenyl)chloroacetoamide [28] and polyphosphate ester (PPE) [52] used in the synthesis of 2-chloromethylbenzoxazole were taken from the literature. A threefold excess of PPE was used to drive the reaction to completion.

2.2. Experimental procedures

2.2.1. Ligand syntheses

2.2.1.1. 2-[(Diphenylphosphinoyl)methyl]-4,5-dihydrooxazole (2).

The precursor phosphane, 2-[(diphenylphosphanyl)methyl]-4,5-dihydrooxazole (**1**), was prepared in a fashion similar to that described in the literature [18]. A sample of 2-methyl-2-oxazoline (2.6 g, 30.8 mmol, Aldrich) in dry THF (5 mL) was added dropwise with stirring (10 min, -78 °C) under dry nitrogen to BuLi in hexane (19.4 mL, 1.6 M, 30.8 mmol) in dry THF (50 mL). Stirring was continued (-78 °C, 1 h) wherein the solution changed from colorless to yellow. A sample of degassed Me₃SiCl (4.0 mL, 30.8 mmol) was added (-78 °C), stirred (1 h) and then Ph₂PCl (5.5 mL, 30.8 mmol) in dry THF (10 mL) was added. The resulting mixture was stirred and allowed to slowly warm to 23 °C (12 h). The volatiles were removed *in vacuo* leaving a yellow oil that was extracted with CH₂Cl₂ (100 mL), concentrated, then vacuum evaporated over several days leaving a yellow solid, **1**. Yield: 3.8 g, 47%. Mp 58–60 °C. HRESI-MS: *m*/*z* 270.1058 [M+H⁺] (C₁₆H₁₇NOP requires 270.0970). ³¹P NMR (CDCl₃): δ = -16.9. ¹H NMR (250 MHz, CDCl₃): δ = 3.0 (s, 2H, *H*₁), 3.6 (t, 2H, *H*₃, ³*J*_{HH} = 9.2 Hz), 3.9 (t, 2H, *H*₄, ³*J*_{HH} = 9.5 Hz), 7.2 (m, 6H, *Ar*), 7.3–7.4 (m, 4H, *Ar*).

The crude sample of $\mathbf{1}$ was dissolved in Et₂O and oxygen was bubbled through the solution (23 °C, 2d). The solvent was evaporated and the yellow oily residue purified by column chromatography (silica gel, 70-230 mesh, elution by CH₂Cl₂/MeOH 95/5 followed by CH₂Cl₂/MeOH 90/10). Compound 2 was obtained as a yellow solid. Yield: 5.1 g, 58%. Mp 128-130 °C. Recrystallization from EtOAc gave colorless single crystals. HRESI-MS: m/ *z* = 286.0993 [M+H⁺] (C₁₆H₁₇NO₂P requires 286.0997); 308.0818 [M+Na⁺]. IR (KBr, cm⁻¹): v = 1659 (s, v_{CN}), 1188 (s, v_{PO}). ³¹P NMR (CDCl₃): δ = 28.1. ¹H NMR (500 MHz, CDCl₃): δ = 3.4 (d, 2H, H₁, ${}^{2}J_{HP} = 14.6 \text{ Hz}$, 3.7 (dt, 2H, H_{3} , ${}^{3}J_{HH} = 9.4 \text{ Hz}$, ${}^{5}J_{HP} = 3.6 \text{ Hz}$), 4.0 (t, 2H, H_{4} , ${}^{3}J_{HH} = 9.5 \text{ Hz}$), 7.4–7.5 (m, 6H, Ar), 7.7–7.8 (m, 4H, Ar). ¹H{³¹P} NMR (500 MHz, CDCl₃): δ = 3.4 (s, 2H, H₁), 3.7 (t, 2H, H₃, ${}^{3}J_{\text{HH}}$ = 9.5 Hz), 4.0 (t, 2H, H_{4} , ${}^{3}J_{\text{HH}}$ = 9.5 Hz), 7.4–7.5 (m, 6H, Ar), 7.8 (d, 4H, Ar). ${}^{13}\text{C}{}^{1}\text{H}$ NMR (62.9 MHz, CDCl₃): δ = 32.5 (d, C_{1} , ${}^{1}J_{CP}$ = 64.2 Hz), 54.8 (s, C_{3}), 68.2 (s, C_{4}), 128.9 (d, Ar, J_{CP} = 12.2 Hz), 131.5 (d, Ar, J_{CP} = 9.7 Hz), 132.4 (d, *i*-Ar, ¹ J_{CP} = 100.9 Hz), 132.5 (d, Ar, $I_{CP} = 2.5$ Hz), 161.4 (d, C_2 , ${}^2I_{CP} = 7.4$ Hz).

2.2.1.2. 2-[(Diphenylphosphinoyl)methyl]benzoxazole (3). Method 1. Phenyl magnesium bromide (30 mL, 2.0 M solution in THF, 20 mL) was added dropwise, with stirring, under dry nitrogen to freshly distilled diethyl phosphite (1.0 mL, 6.5 mmol) in dry THF (10 mL). The temperature rose during the addition and the resulting mixture was refluxed (60 °C, 1 h). A sample of 2-chloromethylbenzoxazole (1.1 g, 6.5 mmol) [28] in dry THF (10 mL) was added (23 °C), and the mixture refluxed (60 °C, 12 h) during which time the color turned from yellow to dark red. The THF was vacuum evaporated and the residue treated with saturated aqueous NH₄Cl (100 mL). The resulting mixture was extracted with CHCl₃ $(3 \times 10 \text{ mL})$ and the filtrate evaporated to dryness leaving a vellow solid. 3. Further purification was accomplished by column chromatography (silica gel 70-230 mesh, MeOH/CH₂Cl₂, 5/95). Yield: 2.1 g, 96%. Mp 160-161 °C. Method 2. This method is similar to that described by Minami [27]. Diisopropylamine (2.2 mL, 16 mmol) and BuLi (1.6 M solution in hexane, 10.2 mL, 16 mmol) were combined in dry THF (15 mL), stirred (-78 °C, 10 min), and the solution added with stirring (-78 °C, 15 min) to 2-methylbenzoxazole (1.1 g, 8 mmol) in THF (10 mL). The resulting yellow solution was combined with diphenylphosphinic chloride (1.5 mL, 8 mmol) and stirred (-78 °C, 1.5 h). The mixture was then quenched with aqueous 1.2 M HCl (-78 °C, 100 mL), extracted with CHCl₃ $(3 \times 20 \text{ mL})$, the combined organic layers washed with saturated aqueous brine solution (100 mL) and dried over Na₂SO₄. The recovered organic phase was vacuum evaporated leaving a yellow residue that was initially purified by column chromatography (silica gel, 70-230 mesh, with elution by CH₂Cl₂ followed by 2.5% MeOH/CH₂Cl₂, 5% MeOH/CH₂Cl₂ and 10% MeOH/CH₂Cl₂). The pale yellow solid, 3, was vacuum-dried and crystallized from MeOH/ CH₂Cl₂ (5:95) or from hot ethyl acetate. Yield: 2.3 g, 84%. Method 3. A solution of LDA prepared from diisopropylamine (4.5 mL, 32 mmol) and BuLi (1.6 M in hexane, 20.5 mL, 33 mmol) in THF (15 mL) was added to a solution of 2-methylbenzoxazole (2.1 g. 16 mmol) in THF (10 mL, -78 °C). The combination was stirred (-78 °C, 15 min) and diphenylphosphine chloride (3.3 mL, 17.6 mmol) was added (-78 °C, 1.5 h, -78 °C). The resulting cold mixture was guenched with aqueous 1.2 M HCl (100 mL), warmed to 23 °C and extracted with CHCl₃ (3 \times 20 mL). The combined organic phases were washed with saturated brine solution (100 mL) and dried over Na₂SO₄. This solution was left exposed

to air (24 h) in order to complete the oxidation of the intermediate phosphine. The product was vacuum evaporated and the crude product purified by column chromatography as described above leading to a pale yellow solid, **3.** Yield: 3.8 g, 72%. HRESI-MS: *m*/*z* = 334.1003 [M+H⁺] ($C_{20}H_{17}NO_2P$ requires 334.0997), 356.0815 [M+Na⁺]. IR (KBr, cm⁻¹): *v* = 1610 (s, *v*_{CN}), 1196 (vs *v*_{PO}). ³¹P NMR (CDCl₃): δ = 27.7. ¹H NMR (250 MHz, CDCl₃): δ = 4.1 (d, 2H, *H*₁, ²*J*_{HP} = 14.5 Hz), 7.2 (m, 2H, *Ar*), 7.3–7.5 (m, 8H, *Ar*), 7.7–7.8 (m, 4H *Ar*). ¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ = 32.8 (d, *C*₁, ¹*J*_{CP} = 63.2 Hz), 110.4 (s), 119.6 (s), 123.9 (s), 124.7 (s), 128.5 (d, *C*₁₀, ²*J*_{CP} = 12.5 Hz), 130.9 (d, *C*₁₁, ³*J*_{CP} = 9.6 Hz), 131.3 (d, *C*₉, ¹*J*_{CP} = 104.3 Hz), 132.1 (d, *C*₁₂, ⁴*J*_{CP} = 2.8 Hz), 141.0 (s), 150.9(s), 158.6 (d, *C*₂, ²*J*_{CP} = 9.1 Hz). ¹³C{¹H, ³¹P}NMR (125.7 MHz, CDCl₃): δ = 32.8, 110.4, 119.6, 124.1, 124.7, 128.5, 130.9, 131.3, 132.2, 141.0, 150.9, 158.6. *Anal.* Calc. for *C*₂₀H₁₆NO₂P: C, 72.07; H, 4.84; N, 4.20. Found: C, 71.16; H, 4.85; N, 3.89%.

2.2.1.3. 2-[(Di-o-tolylphosphinoyl)methyl]benzoxazole (4). A sample of o-tolylmagnesium bromide (2.0 M solution in Et₂O, 6.5 mL, 13.0 mmol) in THF (15 mL) was added dropwise to freshly distilled diethyl phosphite (0.6 g, 4.4 mmol) in THF (10 mL). The temperature rose during the addition and the resulting mixture was refluxed (70 °C, 1 h). The mixture was then cooled (23 °C) and 2-chloromethylbenzoxazole (0.7 g, 4.4 mmol) [28] in THF (10 mL) was added with stirring. The resulting mixture was refluxed (70 °C, 12 h), then cooled (23 °C) and the volatiles removed by vacuum evaporation leaving a yellow residue. The residue was treated with saturated aqueous NH₄Cl (100 mL), extracted with CHCl₃ $(3 \times 20 \text{ mL})$, the combined organic phases dried over Na₂SO₄ and vacuum evaporated. The recovered yellow solid was purified by column chromatography (silica gel 70-230 mesh, elution with EtOAc/hexane (50:50) and then EtOAc (100%)). This left a pale yellow oil that was washed with CH₂Cl₂/hexane mixture and vacuum dried leaving a white solid, 4. Yield: 1.0 g, 67%. Mp 161-162 °C. HRESI-MS: m/z = 362.1304 [M+H⁺] (C₂₂H₂₁NO₂P requires 362.1310. IR (KBr, cm⁻¹): 1607 (s, v_{CN}), 1178 (vs v_{PO}). ³¹P NMR (CDCl₃) δ = 31.1. ¹H NMR (500 MHz, CDCl₃): δ = 2.4 (s, 6H, H₁₁), 4.2 (d, 2H, H₁, ²J_{PH} = 14.2 Hz), 7.2 (m, 6H, Ar), 7.3–7.4 (m, 3H, Ar), 7.5–7.6 (m, 1H, Ar), 7.7–7.8 (d, 2H, H_{15} , ${}^{3}J_{PH}$ = 13.8 Hz). ${}^{1}H{}^{31}P{}$ NMR (500 MHz, CDCl₃): δ = 2.4 (s,6H, H₁₁), 4.2 (s, 2H, H₁), 7.1–7.2 (m, 6H, Ar), 7.3-7.4 (m, 3H, Ar), 7.5 (m, 1H, Ar), 7.7 (s, 2H, H₁₅). ¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ = 21.0 (d, C₁₁, ³J_{CP} = 15.3 Hz), 32.3 (d, C_1 , ${}^{1}J_{CP}$ = 64.8 Hz), 110.4 (s), 119.5 (s), 123.9 (s), 124.6 (s), 125.6 (d, C_{15} , ${}^{2}J_{CP}$ = 12.8 Hz), 130.2 (d, C_{9} , ${}^{1}J_{CP}$ = 100.3 Hz), 131.6 $(d, J_{CP} = 11.8 \text{ Hz}), 131.7 (d, J_{CP} = 11.1 \text{ Hz}), 132.0 (s), 141.0 (s), 141.9$ $(d, C_{14}, {}^{3}J_{CP} = 9.7 \text{ Hz}), 151.1 \text{ (s)}, 159.0 \text{ (d, } C_{2}, {}^{2}J_{CP} = 8.5 \text{ Hz}). Anal. Calc.$ for C₂₂H₂₀NO₂P: C, 73.12; H, 5.58; N, 3.88. Found: C, 72.83; H, 5.66; N, 3.86%.

2.2.1.4. 2-[Bis(2-trifluoromethylphenyl)phosphinoylmethyl]benzoxazole (5). Magnesium turnings (0.5 g, 20.5 mmol) and THF (10 mL) were placed in a nitrogen purged 250 mL Schlenk vessel. 2-Bromobenzotrifluoride (2.8 mL, 20.5 mmol) in THF (10 mL) was added dropwise (23 °C) with stirring. The temperature rose during the addition and the mixture was refluxed (60 °C, 1 h) to complete the reaction. Freshly distilled diethyl phosphite (1.0 mL, 7.5 mmol) in dry THF (10 mL) was added dropwise to the cooled Grignard solution (23 °C) and the mixture was refluxed (60-70 °C, 1 h). The reaction mixture was cooled (23 °C) and freshly distilled 2chloromethylbenzoxazole (1.3 g, 7.5 mmol) in dry THF (10 mL) was added. This mixture was refluxed (12 h) and the progress of the reaction monitored by TLC (95% CH₂Cl₂/5% MeOH). Volatiles were removed by vacuum evaporation and the residue was treated with saturated aqueous NH₄Cl (100 mL) and extracted with CHCl₃ $(3 \times 40 \text{ mL})$. The combined organic phases were dried (Na₂SO₄) and evaporated leaving an orange solid. Crystallization of the solid

from EtOAc/hexane solution provided colorless crystals of **5**. Yield: 2.7 g, 74%. Mp 140–141 °C. HRESI-MS: m/z = 470.0743 [M+H⁺] (C₂₂H₁₅F₆NO₂P requires 470.0744. IR (KBr, cm⁻¹): v = 1616 (s, v_{CN}), 1176 (vs v_{PO}). ³¹P NMR (CDCl₃): $\delta = 28.4$. ¹H NMR (250 Mz, CDCl₃): $\delta = 4.3$ (d, 2H, H_1 , ²J_{PH} = 14.5 Hz), 7.2 (m, 2H, Ar), 7.3–7.4 (m, 1H, Ar), 7.5–7.6 (m, 5H, Ar), 7.7–7.8 (m, 2H, Ar), 8.2–8.3 (m, 2H, Ar). ¹³C{¹H} NMR (125.7 MHz, CDCl₃): $\delta = 34.0$ (d, C_1 , ¹J_{CP} = 89.7 Hz), 110.4 (s), 119.7 (s), 123.4 (q, CF₃, ¹J_{CF} = 273.0 Hz), 124.2 (s), 124.9 (s), 127.6 (s), 130.6 (d, C₉, ¹J_{CP} = 99.3 Hz), 131.5 (d, J_{CP} = 13.8 Hz), 131.8 (qd, C_{10} , ²J_{CP} = 6.5 Hz, ²J_{CF} = 33.5 Hz), 132.4 (s), 134.2 (d, J_{CP} = 8.9 Hz), 141.0 (s) 150.9 (s), 158.3 (d, C₂, ²J_{CP} = 9.6 Hz. Anal. Calc. for C₂₂H₁₄F₆NO₂P: C, 56.30; H, 3.01; N, 2.98. Found: C, 55.79; H, 2.89; N, 2.98%.

2.2.1.5. 2-[Bis(3,5-bis-trifluoromethylphenyl)phosphinoylmethyl]benzoxazole (**6**).

The phosphono Grignard reagent was prepared in the same fashion as described for the synthesis of 5 by using 3,5-bis(trifluoromethyl)bromobenzene (3.5 mL, 20.5 mmol) and diethyl phosphite (1.0 mL, 7.5 mmol). The resulting solution was combined with 2-chloromethylbenzoxazole (1.3 g, 7.5 mmol) in THF (10 mL) and refluxed (50–60 °C, 12 h). The dark red solution was vacuum evaporated and the residue treated with saturated aqueous NH₄Cl (100 mL), extracted with CHCl₃ (3×40 mL), the combined organic phases dried (Na₂SO₄) and vacuum evaporated leaving an orange solid. The solid was crystallized from EtOAc/hexane solution leaving colorless crystals of 6. Yield 2.6 g, 55%. Mp 209–211 °C. HRESI-MS: $m/z = 606.0496 [M+H^+] (C_{24}H_{13}F_{12}NO_2P re$ quires 606.0492. IR (KBr, cm⁻¹): 1616 (s, v_{CN}), 1175 (sh), 1140 (s, v_{PO}). ³¹P NMR (CDCl₃): δ = 23.4. ¹H NMR (250 Mz, CDCl₃): δ = 4.2 (d, 2H, H_1 , ${}^2J_{HP}$ = 16.2 Hz), 7.2–7.3 (m, 3H, Ar), 7.6 (m, 1H, Ar), 8.1 (a, 21, 11, J_{HP}^{-1} 10.2 Hz), 7.2 7.5 (iii, 51, 74), 7.6 (iii, 11, 74), 6.1 (s, 2H, H_{13}), 8.4 (d, 4H, H_{10} , ${}^{3}J_{HP}$ = 11.8 Hz). ${}^{13}C{}^{1}H$ NMR (125.7 Mz, CDCl₃): δ = 32.7 (d, C_{1} , ${}^{1}J_{CP}$ = 67.6 Hz), 110.4 (s), 120.0 (s), 122.5 (q, CF_{3} , ${}^{1}J_{CF}$ = 273.5 Hz), 124.9 (s), 125.8 (s), 126.8 (s), 131.5 (d, C_{10} , ${}^{2}J_{CP}$ = 8.4 Hz), 132.7 (qd, C_{11} , ${}^{3}J_{CP}$ = 12.4 Hz, ${}^{2}J_{CF}$ = 34.6 Hz), 133.5 (d, C_9 , ${}^{1}J_{CP}$ = 102.3 Hz), 140.7 (s), 150.7 (s), 156.4 (d, C_2 , $^{2}J_{CP}$ = 7.7 Hz). Anal. Calc. for C₂₄H₁₂F₁₂NO₂P: C, 47.62; H, 2.00; N, 2.31. Found: C. 47.70: H. 2.05: N. 2.28%.

2.2.2. Synthesis of lanthanide complexes

2.2.2.1. [*Nd*(**2**)₂(*NO*₃)₃(*CH*₃*OH*)]. A sample of **2** (0.5 g, 1.7 mmol) in MeOH (5 mL) was combined with Nd(NO₃)₃·6H₂O (0.26 g, 0.58 mmol) in MeOH (2 mL), stirred (10 min), and a white precipitate formed. Stirring was continued (1 h) and the solid collected by filtration, washed with cold MeOH and dried (0.44 g, 54%). The complex was isolated as [Nd(**2**)(NO₃)₃(MeOH)] by dissolving a sample in a minimum of hot MeOH followed by slow cooling. This provided X-ray quality crystals of the complex. IR (KBr, cm⁻¹): v = 1646 (s, v_{CN}), 1160 (s, v_{PO}). Anal. Calc. for C₃₃H₃₆N₂NdO₁₄P₂: C, 42.49; H, 3.89; N, 7.51; Nd, 15.46; P, 6.64. Found: C, 42.32; H, 3.73; N, 7.47; Nd, 15.60; P, 6.27%.

2.2.2.2. $[Nd(2)_2(NO_3)_3]$. A sample of $[Nd(2)(NO_3)_3(CH_3OH)]$ was dissolved in CH₃CN, stirred (12 h) and the volatiles removed by vacuum evaporation. The remaining white solid was dissolved in a minimum of CH₃CN and the solution allowed to slowly evaporate (5 d) leaving colorless crystals of $[Nd(2)_2(NO_3)]$ suitable for X-ray diffraction analysis.

2.2.2.3. $[Nd(3)_2(NO_3)_3] \cdot 3(CHCl_3)$. A sample of **3** (0.1 g, 0.3 mmol) was dissolved in MeOH (5 mL) and combined with Nd(NO₃)₃·6H₂O (0.06 g, 0.15 mmol) in MeOH (2 mL). The mixture was stirred (12 h) resulting in a clear solution which was allowed to slowly evaporate (4 d). A white solid formed and this was crystallized from hot CHCl₃ from which colorless single crystals were isolated (0.15 g, 79%). IR (KBr, cm⁻¹): v = 1155 (s, v_{PO}). Anal. Calc. for

 $[Nd(\mathbf{3})_2(NO_3)_3]\cdot 3(CHCl_3), \ C_{42.5}H_{34.5}Cl_{7.5}N_5NdO_{13}P_2; \ C, \ 38.11; \ H, \ 2.60; \ N, \ 5.17. \ Found: \ C, \ 42.33; \ H, \ 3.04; \ N, \ 6.21\%.$

2.2.2.4. $[Yb(3)_2(NO_3)_3(H_2 O)] \cdot 0.5(CH_3OH)$. A sample of **3** (0.13 g, 0.39 mmol) dissolved in MeOH (5 mL) and $Yb(NO_3)_3 \cdot 5H_2O$ (0.08 g, 0.2 mmol) in MeOH (5 mL) were combined and stirred (23 °C, 12 h). The solution was then evaporated and the colorless residue dissolved in CHCl₃/hexane which led to the formation of yellow crystals (0.11 g, 52%). IR (KBr, cm⁻¹): v = 1159 (s, v_{PO}). Anal. Calc. for $[Yb(3)_2(NO_3)_3(H_2O)] \cdot 0.5(CH_3OH)$, $C_{42.5}H_{36}N_5O_{14.5}P_2Yb$: C, 45.90; H, 3.42; N, 6.61. Found: C, 47.90; H, 3.83; N, 5.79%.

2.2.2.5. [Yb(**4**)₂(NO₃)₃(H₂O)]. A sample of **4** (0.2 g, 0.55 mmol) in MeOH (10 mL) and Yb(NO₃)₃·5 H₂O (0.12 g, 0.28 mmol) in MeOH (2 mL) were combined and stirred (23 °C, 12 h). The solution was evaporated leaving a yellow solid that was recrystallized from MeCN/MeOH solution leaving colorless crystals (0.26 g, 85%). IR (KBr, cm⁻¹): v = 1151 (s, v_{PO}). Anal. Calc. for [Yb(**4**)(NO₃)₃(H₂O)], C₄₄H₄₂N₅O₁₄P₂Yb: C, 48.04; H, 3.81; N, 6.36. Found: C, 44.73; H, 3.67; N, 6.38%.

2.2.2.6. $[Nd(4)_2(NO_3)_3(H_2O)]$. A sample of **4** (0.2 g, 0.55 mmol) in MeOH (10 mL) and Nd(NO₃)₃·6H₂O in MeOH (10 mL) were combined and stirred (23 °C, 12 h). Solvent was evaporated leaving a pale yellow solid. X-ray quality crystals were obtained by slow evaporation of a MeOH/EtOAc solution. IR (KBr, cm⁻¹): v = 1152 (s, v_{PO}). Anal. Calc. for [Nd(**4**)(NO₃)₃(H₂O)], C₄₄H₄₂N₅NdO₁₄P₂: C, 49.34; H, 3.92; N, 6.53. Found: C, 44.74; H, 3.63; N, 6.83%.

2.2.2.7. $[Yb(5)_2(NO_3)_3(H_2 O)] \cdot 0.5(CH_3CN)$. A sample of **5** (0.2 g, 0.43 mmol) in MeOH (10 mL) and Yb(NO_3)_3 \cdot 5H_2O in MeOH (2 mL) were combined and stirred (23 °C, 12 h). The solution was evaporated leaving a white solid that was crystallized from MeCN (0.18 g, 64%). IR (KBr, cm⁻¹): v = 1176 (s, v_{PO}). Anal. Calc. for $[Yb(5)_2(NO_3)_3(H_2O)] \cdot 0.5(CH_3CN)$, $C_{45}H_{31.5}$ $F_{12}N_{5.5}O_{14}P_2Yb$: C,40.44; H, 2.35; N, 5.76. Found: C, 37.53; H, 2.63; N, 5.84%.

2.3. Single crystal X-ray diffraction analyses

Single crystals of the ligands, **2**, **3**, **4** and **5**, and complexes $[Nd(2)_2(NO_3)_3(CH_3OH)]$, $[Nd(2)_2(NO_3)_3]$, $[Yb(3)_2(NO_3)_3(H_2O)] \cdot 0.5$

Table 1Crystallographic data for ligands 2–5.

(CH 3OH), Nd(4)(NO3)3(H2O)], [Yb(4)2(NO3)3(H2O)], [Yb (5)2(NO3)3 (H_2O)]·0.5(CH₃CN) and [Nd(**3**)₂(NO₃)₃]·3(CHCl₃), were placed in glass capillaries and sealed. Crystal data were collected on a Bruker X8 Apex 2 CCD-based X-ray diffractometer, outfitted with an Oxford Cryostream 700 low temperature device, by using Mo Ka radiation (0.71073 Å). The data frames were integrated with Bruker SAINT [53] and processed with SADABS [54]. In all cases, a full sphere of data was collected with negligible decay. Lattice parameters and data collection details are presented in Tables 1 (ligands) and Table 2 (complexes). The structures were solved and refined with Bruker SHELXTL [55]. All non-hydrogen atoms were refined anisotropically and H-atoms were placed in ideal positions and refined with $U_{iso} = 1.2 U_{eq}$ of the parent atom except as noted otherwise. In compound 4 the hydrogen atoms on aromatic C atoms were included in ideal positions with fixed $U_{iso} = 1.2 U_{eq}$ while the H-atoms on the terminal methyl groups were placed in ideal positions with $U_{iso} = 1.5 U_{eq}$. For $[Nd(2)_2(NO_3)_3(CH_3OH)]$ the nonhydrogen atoms were refined anisotropically except for C33 of the inner coordination sphere CH₃OH. The atom was disordered over three positions, and it was refined isotropically with fixed occupancies (C33, 39%, C33', 34%, C33", 27%). The CH₃OH OH-atom was located and refined in position and U_{iso} , and the methyl Hatoms were refined with $U_{iso} = 1.5 U_{eq}$. The other H-atoms were placed in idealized positions and refined with $U_{iso} = 1.2 U_{eq}$ of the parent atom. For $[Nd(2)_2(NO_3)_3]$ the H-atoms were placed in idealized positions and refined isotropically with $U_{iso} = 1.2 U_{eq}$ of the parent atom except for the H-atoms on C1 and C21. These were allowed to vary in position and U_{iso} . In $[Yb(3)_2(NO_3)_3] \cdot 0.5(CH_3OH)$ there is a disordered outer sphere CH3OH molecule that resides close to a center of symmetry and is at half occupancy. The methyl H-atoms and the OH H-atom were fixed in ideal positions with $U_{iso} = 1.2 U_{eq}$ and 1.5 U_{eq} , respectively. The H-atoms on the water molecule were located in the difference maps and refined with variable position and Uiso. In [Nd(3)2(NO3)3]·3(CHCl3)there are three CHCl₃ solvent molecules in the asymmetric unit. Two are ordered but the third is disordered over two sites [C43–Cl7. Cl8. Cl9 and C44-Cl10. Cl11. Cl12] with occupancies 0.47 and 0.53. The H-atoms were included in ideal positions with fixed $U_{iso} = 1.2$ U_{eq} of the parent atom. For $[Nd(4)_2(NO_3)_3(H_2O)]$ one tolyl ring [C38-C44] showed signs of disorder that could not be adequately modeled, and it was constrained as a regular hexagon with the

	2	3	4	5
Empirical formula	C ₁₆ H ₁₆ NO ₂ P	C ₂₀ H ₁₆ NO ₂ P	C ₂₂ H ₂₀ NO ₂ P	$C_{22}H_{14}F_6NO_2P$
Color, habit	colorless block	colorless plate	colorless prism	colorless prism
Crystal size (mm)	$0.46 \times 0.44 \times 0.42$	$0.16 \times 0.41 \times 0.46$	$0.23\times0.35\times0.47$	$0.25\times0.39\times0.41$
Formula weight	285.27	333.31	361.36	469.31
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	P212121	$P2_1/n$	$P2_1/c$	$P2_1/n$
Unit cell dimension				
a (Å)	8.3623(6)	8.7818(3)	8.4150(5)	13.9184(7)
b (Å)	11.2530(8)	18.4043(6)	18.982(1)	9.2015(5)
<i>c</i> (Å)	15.539(1)	10.7928(3)	11.5290(6)	15.9039(8)
α (°)	90	90	90	90
β (°)	90	109.015(2)	98.419(2)	99.313(2)
γ (°)	90	90	90	90
Volume	1462.3(2)	1649.18(9)	1821.7(2)	2010.0(2)
Ζ	4	4	4	4
<i>T</i> (K)	223(2)	223(2)	225(2)	225(2)
Density (g cm ⁻³)	1.296	1.342	1.318	1.551
Absorption coefficient (mm ⁻¹)	0.188	0.178	0.167	0.212
Minimun/maximum transmission	0.910/0.920	0.920/0.970	0.920/0.960	0.916/0.946
Reflection collected	39 352	40 488	74 096	54 342
Independent reflections [R _{int}]	4691[0.0182]	6066[0.0225]	6263[0.0243]	6777[0.0196]
Final R indices $[I > 2\sigma(I)] R_1(wR_2)$	0.0275(0.0649)	0.0406(0.1149)	0.0384(0.1076)	0.0415(0.1194)
Final R indices (all data) R ₁ (wR ₂)	0.0287(0.0657)	0.0495(0.1239)	0.0440(0.1141)	0.0507(0.1296)

Crystallographic data for coordination complexes.	Table 2
	Crystallographic data for coordination complexes.

	•						
	$[Nd(2)_2(NO_3)_3(CH_3OH)]$	$[Nd(2)_2(NO_3)_3]$	$[Yb(3)_2(NO_3)_3(H_2O)] \cdot 0.5(CH_3OH)$	$[Yb(4)_2(NO_3)_3(H_2O)]$	$[Nd(4)_2(NO_3)_3(H_2O)]$	$[Yb(5)_2(NO_3)_3(H_2O)] \cdot 0.5(CH_3CN)$	$[Nd(3)_2(NO_3)_3]\cdot 3(CHCl_3)$
Empirical formula	C33H36N5NdO14P2	$C_{32}H_{32}N_5NdO_{13}P_2$	C _{40.5} H ₃₆ N ₅ O _{14.5} P ₂ Yb	$C_{44}H_{42}N_5O_{14}P_2Yb$	$C_{44}H_{42}N_5NdO_{14}P_2$	$C_{45}H_{31.5}F_{12}N_{5.5}O_{14}P_2Yb$	$C_{43}H_{35}Cl_9N_5NdO_{13}P_2$
Color, habit	colorless plate	colorless prism	pink block	colorless prism	pale blue prism	colorless prism	colorless prism
Crystal size (mm)	$0.27\times0.23\times0.21$	$0.15 \times 0.46 \times 0.52$	$0.32 \times 0.32 \times 0.50$	$0.46 \times 0.25 \times 0.14$	$0.53 \times 0.37 \times 0.0.35$	$0.19 \times 0.35 \times 0.39$	$0.09 \times 0.26 \times 0.30$
Formula weight	932.85	900.81	1059.72	1099.81	1071.01	1336.24	1354.99
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	triclinic
Space group	$P2_1/n$	ΡĪ	$P2_1/n$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	P2 ₁ /c	ΡĪ
Unit cell dimension							
a (Å)	16.0073(9)	12.1596(4)	10.0465(8)	10.6206(6)	10.698(1)	11.8234(6)	13.1425(3)
b (Å)	12.3024(7)	13.5689(4)	20.238(2)	11.6896(7)	11.714(1)	15.7990(8)	13.8228(3)
<i>c</i> (Å)	19.197(1)	13.8678(5)	21.291(2)	37.538(2)	37.928(5)	26.812(1)	17.8614(5)
α (°)	90	63.326(1)	90	90	90	90	96.368(1)
β (°)	97.846(2)	76.159(1)	94.132(3)	90	90	92.062(2)	110.695(2)
γ (°)	90	64.092(1)	90	90	90	90	111.438(1)
Volume	3745.0(4)	1836.4(1)	4317.6(6)	4660.4(5)	4753(1)	5005.2(4)	2715.9(1)
Ζ	4	2	4	4	4	4	2
T (K)	223(2)	228(2)	223(2)	225(2)	225(2)	225(2)	223(2)
Density (g cm ⁻³)	1.654	1.629	1.630	1.567	1.497	1.773	1.657
Absorption coefficient (mm ⁻¹)	1.546	1.571	2.314	2.146	1.229	2.049	1.521
Minimum/maximum transmission	0.660/0.720	0.464/0.796	0.391/0.525	0.430/0.750	0.560/0.650	0.501/0.698	0.659/0.876
Reflection collected	99906	60847	158885	183428	150752	178785	93947
Independent reflections [R _{int}]	10925[0.0216]	14894[0.0187]	19173[0.0317]	18864[0.0505]	18473[0.0441]	21100[0.0263]	20616[0.0458]
Final <i>R</i> indices $[I > 2\sigma (I)] R_1$ (wR_2)	0.0175(0.0435)	0.0203(0.0492)	0.0312(0.0736)	0.0366(0.0829)	0.0400(0.1004)	0.0310/0.0708	0.0408(0.10940)
Final R indices (all data) $R_1(wR_2)$	0.0199(0.0457)	0.0242(0.0526)	0.0397(0.0793)	0.0415(0.0851)	0.0431(0.1022)	0.0471/0.0822	0.0575(0.1028)

methyl group allowed to vary in position. The H-atoms on the water molecule were located in the final difference map but they were fixed in position with an O-H distance 0.83 Å. All H-atoms were included in ideal positions with fixed $U_{iso} = 1.2 U_{eq}$ of the parent atom except for the H-atoms on the water and the terminal methyl with U_{iso} = 1.5. The Flack parameter for $[Yb(4)_2(NO_3)_3(-$ H₂O)] converged to 0.349(6) suggesting that the complex is a racemic twin. There are no signs of disorder; however, the tolyl ring has a large range of C-C bond lengths so the ring was constrained as a regular hexagon in the final refinement. The H-atoms were included in ideal positions with fixed $U_{iso} = 1.2 U_{eq}$ of the parent atom except for the hydrogen atoms on the terminal methyl and water which were set to $U_{iso} = 1.5 U_{eq}$ of the parent atom. In $[Yb(5)_2(-$ NO₃)₃(H₂O)] 0.5(CH₃CN), the CH₃CN molecule is close to a center of symmetry and is at half-occupancy. The H-atoms were placed in ideal positions and refined with $U_{iso} = 1.2 U_{ea}$ of the parent atom.

3. Results and discussion

3.1. Ligand syntheses and characterization

The synthesis of **I** (R = Ph, **2**) was accomplished in a manner described by Braunstein and coworkers [18] as summarized in Scheme 1. The intermediate phosphine, **1**, was recovered in lower yield (47%) than previously described, but the physical properties and spectroscopic data are identical to those reported. No evidence for the formation of the bis-(phosphinomethyl)oxazoline was noted. The P-oxidation of **1** to form **2** was initially attempted by addition of aqueous H_2O_2 and *m*-CPBA/CHCl₃ solutions at 23 °C. However, these conditions proved to be too harsh, and phosphine oxidation was performed by bubbling oxygen gas through an Et₂O solution of **1**. The reaction is slow but efficient when performed on a 2 g scale. The product **2** was isolated and purified, with some loss,



Scheme 1.

as a pale yellow solid via column chromatography. The CHN analytical data and ¹H NMR spectra suggest the presence of a minor impurity that displays at least one unique proton resonance at 7.28 ppm. Compound **2** may be obtained analytically pure by recrystallization from hot EtOAc. The compound displays an intense [M+H⁺] ion in the HRESI-MS and strong infrared bands at 1659 and 1188 cm⁻¹ that are assigned to v_{CN} and v_{PO} , respectively. The ³¹P NMR spectrum of **2** shows a single resonance at δ 28.1 that is, as expected, downfield of the resonance for the phosphine **1**, δ –16.9. Preparation of **2** in a one-step procedure by use of Ph₂P(O)Cl in place of Ph₂PCl was explored, but **2** was obtained only in low yield along with several unidentified species.

Although we were initially interested in preparing several organyl derivatives of 2, the sensitivity of the molecule to aqueous acid led us to shift attention to the preparation of previously unreported 2-[(phosphinoyl)methyl]benzoxazoles, J, that were expected to be more robust. The synthesis of J (R = Ph, 3) was accomplished via three methods summarized in Scheme 2. Although it requires preparation of commercially unavailable 2-(chloromethyl)benzoxazole (two steps from 2-aminophenol [28]), the phosphino-Grignard approach (method 1) proved to be the most efficient of the three procedures. Furthermore, since a variety of phosphino-Grignard reagents are easily prepared from diethylphosphite and RMgCl or RMgBr reagents [56-61], method 1 was also used to prepare 4-6. The optimized yield of 3 was 96% while the unoptimized yields for 4-6 were 55-74% based on 2-(chloromethyl)benzoxazole. The one-step synthesis of 3 via method 2 (Scheme 2) is related to a reaction reported by Minami and coworkers [27] for the synthesis of the diethyl phosphonate, J (R = OEt). The yield of **3** by this route is good (84%); however, application of the chemistry for the synthesis of other derivatives requires preparation of the respective R₂P(O)Cl reagents. Method 3 employs chlorodiphenyl phosphine and 2-(methylbenzoxazole in a Minami-like synthesis related to the procedure shown in Scheme 1. The yield of **3** from this approach is good (72%), but its application to other derivatives requires chlorodiorganyl phosphines that are generally expensive or commercially unavailable. Lastly, it is noted that Kosaka and Wakabayashi [28] reported the formation of J (R = OEt) from an Arbusov reaction of 2-(chloromethyl)benzoxazole and P(OEt)₃ at 150 °C. In our hands, the Arbusov methodology did not provide a good approach for synthesis of **3–6**.

Scheme 2.

The new ligands, **3–6**, were obtained as analytically pure solids that exhibit strong parent, [M+H⁺], and sodium complex, [M+Na⁺], ions in the HRESI-MS. Infrared spectra display strong adsorptions in the regions 1616–1607 and 1196–1175 cm^{-1} that are tentatively assigned to v_{CN} and v_{PO} stretching vibrations, respectively. The decrease in $v_{\rm CN}$ relative to the value recorded for **2** (1659 cm⁻¹) is expected as a result of C=N bond delocalization with the fused aromatic ring system. The ³¹P NMR spectra show a single resonance in the region δ 23.4–31.1. This chemical shift region is characteristic for aryl phosphine oxides [41,44,56] and CF₃ decorated aryl phosphine oxides [48,59,60]. The ¹H and ¹³C NMR spectra are complex, but a majority of the observed resonances were assigned in detail by a combination ¹H and ³¹P coupled and decoupled experiments along with comparisons with spectra for [(phosphinovl)methylpyridine N-oxides compounds related [45.48.56.59]. The spectra for **3–6** are included in Supplementary material. It is noted that the "elbow" methyl groups spanning the $R_2P(O)$ group and the benzoxazole ring show little variation with R group modifications: ¹H δ 4.1–4.2, J_{PH} = 14.2–16.2 Hz; ¹³C{¹H} δ 32.3–34.0, J_{CP} = 63.2–69.4 Hz.

3.2. Ligand X-ray crystal structure determinations

The molecular structures for the ligands **2–5** have been confirmed by single crystal X-ray diffraction analyses. Views of the molecules are shown in Figs. 1-4 and selected bond lengths are summarized in Table 3. The molecular structure of 2 consists of a planar 4,5-dihydroxazole ring bonded at the 2-position (C3) to a diphenylmethyl phosphine oxide arm. The P=O bond vector is twisted out of the ring plane as indicated by the torsion angle 01-P-C4-C3, 60.8(1)°. The P-O1 bond length, 1.4865(8) Å, is comparable with related distances in 2-[(diphenylphosphinoyl)methyl] pyridine and pyridine N-oxide ligands [45,59], and it is consistent with a localized P=O double bond. The C-N bond lengths, C3-N, 1.253(2) Å and C2–N, 1.475(2) Å, indicate a localized C=N double bond and a C-N single bond, respectively, in the dihydrooxazoline ring. The shorter distance is comparable with the C=N bond length in the phosphine ligand, 2-[1-(diphenylphosphanyl)ethyl]-4,4-dimethyl-4,5-dihydrooxazole, 1.259(3) Å [25]. The difference between the two C-O bond lengths in the dihydrooxazole ring is less pronounced but still significant: C3-O2, 1.344(2) Å and C1-O2, 1.448(2) Å. It is noted that in the unit cell the molecular units of **2** show alignment along the *b*-axis probably as a result of weak hydrogen bonding between the phosphoryl O-atom and dihydrooxazoline O-atom in each molecule with arvl ring C-H H-atoms in neighboring molecules, e.g., in C6-H6···O2(#1): H6···O2(#1),



Fig. 1. Molecular structure and atom labeling scheme for 2. Thermal ellipsoids are shown at the 20% level.



Fig. 2. Molecular structure and atom labeling scheme for 3. Thermal ellipsoids are shown at the 20% level.



Fig. 3. Molecular structure and atom labeling scheme for 4. Thermal ellipsoids are shown at the 20% level.



Fig. 4. Molecular structure and atom labeling scheme for 5. Thermal ellipsoids are shown at the 20% level.

Table 3	
Selected bond lengths (Å) in ligands 2-5	

Bond Type	2	3	4	5
P-O	P-01 1.4865(8)	P1-01 1.4831(8)	P1-O2 1.4892(8)	P-02 1.4714(9)
P-C	P-C4 1.823(1)	P1-C8 1.823(1)	P1-C8 1.833(1)	P- C8 1.830(1)
	P-C5 1.804(1)	P1-C9 1.798(1)	P1-C9 1.807(1)	P-C9 1.828(1)
	P-C11 1.799(1)	P1-C15 1.806(1)	P1-C16 1.807(1)	P-C16 1.817(1)
C-N	C3-N 1.253(2)	C1-N1 1.293(2)	C7-N1 1.293(1)	C7-N1 1.291(2)
	C2-N 1.475(1)	C7-N1 1.397(1)	C1-N1 1.400(1)	C6-N1 1.400(2)
C-0	C3-O2 1.344(2)	C1-O2 1.357(1)	C7-O1 1.363(1)	C7-01 1.352(2)
	C1-O2 1.448(2)	C2-O2 1.383(1)	C3-O1 1.380(1)	C1-O1 1.384(1)
C-C	C1-C2 1.514(2)	C2-C7 1.379(2)	C1-C6 1.383(2)	C1-C6 1.479(2)
	C3-C4 1.489(2)	C1-C8 1.481(2)	C7-C8 1.481(1)	C7-C8 1.482(2)

2.58 Å, C6···O2(#1), 3.437(2) Å, C6–H6–O2(#1), 151.1°; in C16– H16···O1(#2): H16···O1(#2), 2.49 Å, C16···O1(#2), 3.403(1) Å, C16–H16···O1(#2), 165.4°.

The molecular structures of the benzoxazole-based ligands, 3-5, are similar to each other and to the structure of 2. Each contains a planar benzoxazole ring fragment with the diarylmethylphosphine oxide "arm" bonded at the 2-position (2, C1; 3, C7, 4, C7). The P=O bond vector is rotated out of the benzoxazole ring plane with O-P-C-C torsion angles similar to that found in 2:3, O1-P1-C8-C1, 60.4(1)°; 4, O2-P1-C8-C7, 30.03(9)° and 5, O2-P-C8-C7, 50.6(1)°. The P=O bond lengths in **3** and **4**, 1.4831(8) and 1.4892(8) Å, are similar to the P=O bond length in 2 while the P=O bond length in 5 is noticeably shorter, P-O2, 1.4714(9)Å. We have observed similar P=O bond shortening in other 2-CF₃ decorated aryl phosphine oxides [48,59,60]. Furthermore, there are two nonbonded P...F distances in 5, 2.934 and 3.080 Å, that are shorter than the sum of covalent radii: 3.27 Å [63], and similar interactions at the backside of the phosphoryl P-atom have been observed previously [48,59,60]. It is not clear whether nonbonded P...F interactions or through-bond electron withdrawal or a combination of both effects are responsible for the shorter P=O bond distances in the 2-CF₃ aryl decorated ligands. As found in the structure of 2, the C-N and C-O bond lengths in 3-5 fall into short and long groups, but the differences are much smaller consistent with greater electron delocalization in the benzoxazole systems. Lastly, it is mentioned that a crystal structure determination for 6 was completed; however, the molecule shows severe disorder in one CF₃ group so the data are not included, in full, in this report. It is noted that the P=O bond length, 1.482(1) Å, is more similar to those in **3** and **4**, and short backside $P \cdots F$ interactions involving the ordered *meta*-CF₃ groups are absent.

3.3. Lanthanide ion coordination chemistry and X-ray crystal structure determinations

As mentioned in the Introduction, our primary interest in I and J rests on the nature of the binding interactions displayed by each ligand with hard lanthanide ion acceptors. Namely, do these ligands act only as monodentate PO donors or do they form bidentate PO,N chelate interactions? Therefore, the coordination chemistry of 2-5 toward an early lanthanide, Nd(NO₃)₃·6H₂O, and a late lanthanide, $Yb(NO_3)_3 \cdot 6H_2O$, was explored with 1:1-3:1 ligand:Ln reactant ratios in methyl alcohol solution. The resulting complexes were then crystallized under various conditions (see Section 2). In all cases, even with a deficiency of ligand, the analytical data for the isolated complexes best fit a 2:1 ligand/Ln(III) composition although in some cases the agreement between proposed and experimental compositions is not within 3%. This appears to be due to the loss of outer sphere solvent during handling. The 2:1 composition for the crystalline complexes was confirmed ultimately by X-ray crystal structure determinations, vide infra. It is noted that crystal structures for complexes containing ligand **6** are not presented due to poor crystal quality and/or severe unresolved disorder in the CF_3 groups and outer sphere solvent molecules.

The 2:1 combination of methanol solutions of 2 and Nd(NO₃)₃·6H₂O at 23 °C led to the formation of a slightly soluble white solid. Dissolution of the solid in hot methanol followed by slow cooling resulted in the deposition of crystallographic quality single crystals for which CHN analyses suggest a composition $[Nd(2)_2(NO_3)_3(CH_3OH)]$. Infrared spectra for the complex in KBr pellets show bands at 1646 and 1160 cm⁻¹ that are tentatively assigned to $v_{\rm CN}$ and $v_{\rm PO}$, respectively. The down-frequency coordination shift for the phosphoryl stretching mode, $\Delta v_{PO} = 28 \text{ cm}^{-1}$, is consistent with Nd(III) ion binding to the phosphoryl oxygen atom and the value is comparable to shifts observed for lanthanide ion binding with ligand types **C-E** [38–46,56]. The small perturbation of the v_{CN} mode, $\Delta v_{CN} = 12$ cm⁻¹, suggests that the oxazoline ring N-atom may not be bonded or is weakly bonded to the Nd(III). An X-ray crystal structure determination for the complex confirmed the composition proposed from the elemental analysis. A view of the complex is shown in Fig. 5 and selected bond lengths are summarized in Table 4. The structure solution reveals an unexpected and somewhat unusual coordination condition for two identical neutral ligands bonded to a Nd(III) ion. One ligand is bonded in a bidentate mode, via P=O and Nova-ring/Nd interactions, while the second ligand is coordinated with a monodentate, P=O/Nd interaction. The Noxa-ring atom in the second ligand molecule, however, is hydrogen bonded with the H-atom of an inner sphere methanol molecule. The resulting O14-H14...N2 interaction is nearly linear, 175(3)°, with distances O14-H14, N2-H14, and 014...N2 0.71(2), 1.96(2) and 2.667(2) Å, respectively. This



Fig. 5. Molecular structure and atom labeling scheme for $[Nd(2)_2(NO_3)_3(MeOH)]$. H-atoms, except on the O-atom of MeOH, omitted for clarity. Thermal ellipsoids are shown at the 20% level.

Table 4	
Selected bond lengths (Å) in complexes.	

Bond type	$[Nd(2)_2(NO_3)_3(CH_3OH)]$	$[Nd(2)_2(NO_3)_3]$	$[Yb(3)_2(NO_3)_3(H_2O)] \cdot 0.5(CH_3OH)$	$[Yb(4)_2(NO_3)_3(H_2O)]$	$[Nd(4)_2(NO_3)_3(H_2O)]$	$[Yb(5)_2(NO_3)_3(H_2O)] \cdot 0.5(CH_3CN)$	$[Nd(3)_2(NO_3)_3]\cdot 3(CHCl_3)$
M-OP	Nd-O1 2.4274(9)	Nd-O1 2.3803(9)	Yb-O1 2.228(1)	Yb-O1 2.233(2)	Nd-O1 2.3531(9)	Yb-O1 2.269(1)	Nd-01 2.404(2)
	Nd-O3 2.4136(9)	Nd-O2 2.4189(9)	Yb-O3 2.213(1)	Yb-O3 2.234(2)	Nd-O3 2.350(1)	Yb-O3 2.249(1)	Nd-03 2.420(2)
M-N	Nd-N1 2.655(1)	Nd–N1 2.660 (1) Nd–N2 2.691(1)					Nd–N1 2.665(2) Nd–N2 2.672(2)
M–O _{nitrate}	2.601	2.584	2.426	2.431	2.541	2.414	2.579
avg range	2.549(1)-2.649(1)	2.502(1)-2.703(1)	2.363(2)-2.509(2)	2.369(3)-2.513(3)	2.500(3)-2.579(3)	2.354(2)–2.447(2)	2.530(2)–2.617(3)
M-O _{solvent}	Nd-014 2.447(1)		Yb-05 2.278(2)	Yb-014 2.285(3)	Nd-014 2.427(5)	Yb-05 2.311(2)	
Р-О	P1-O1 1.497(1)	P1-O1 1.496(1)	P1-O1 1.491(1)	P1-O1 1.494(2)	P1-O1 1.498(2)	P1-O1 1.497(2)	P1-O1 1.498(2)
	P2-O3 1.497(1)	P2-O3 1.5015(9)	P2-O3 1.496(2)	P2-O3 1.495(2)	P2-O3 1.504(2)	P2-O3 1.494(2)	P2-O3 1.496(2)
P–C	P1-C1 1.811(1)	P1-C1 1.799(1)	P1-C8 1.817(2)	P1-C8 1.839(3)	P1-C8 1.834(3)	P1-C8 1.833(3)	P1-C8 1.815(2)
	P1-C5 1.793(1)	P1-C5 1.785(1)	P1-C9 1.794(2)	P1-C9 1.787(3)	P1-C9 1.784(3)	P1-C14 1.811(2)	P1-C9 1.792(2)
	P1-C11 1.793(2)	P1-C11 1.796(2)	P1-C15 1.781(2)	P1-C16 1.799(3)	P1-C16 1.804(3)	P1-C21 1.822(2)	P1-C15 1.789(3)
	P2-C17 1.819(1)	P2-C17 1.812(1)	P2-C28 1.813(2)	P2-C30 1.826(3)	P2-C30 1.826(3)	P2-C30 1.828(2)	P2-C28 1.818(2)
	P2-C21 1.797(1)	P2-C21 1.788(1)	P2-C29 1.791(2)	P2-C31 1.794(4)	P2-C31 1.799(4)	P2-C36 1.820(2)	P2-C29 1.787(2)
	P2-C27 1.794(1)	P2-C27 1.792(1)	P2-C35 1.781(2)	P2-C38 1.785(2)	P2-C38 1.775(2)	P2-C43 1.813(2)	P2-C35 1.785(2)
N–C	N1-C2 1.271(2)	N1-C2 1.275(2)	N1-C1 1.286(3)	N1-C7 1.279(4)	N1-C7 1.288(4)	N1-C7 1.275(4)	N1-C7 1.289(3)
	N1-C3 1.484(2)	N1-C4 1.476(2)	N1-C7 1.401(3)	N1-C6 1.402(5)	N1-C6 1.399(4)	N1-C6 1.414(4)	N1-C6 1.404(3)
	N2-C18 1.264(2)	N2-C18 1.274(2)	N2-C21 1.291(3)	N2-C29 1.290(5)	N2-C29 1.287(4)	N2-C29 1.290(3)	N2-C27 1.291(3)
	N2-C19 1.472(2)	N2-C20 1.482(2)	N2-C27 1.407(3)	N2-C28 1.385(5)	N2-C28 1.394(4)	N2-C28 1.399(3)	N2-C26 1.404(3)
0–C	02-C2 1.347(2)	03-C2 1.337(2)	02-C1 1.363(3)	02-C1 1.380(5)	02–C1 1.384(5)	02-C7 1.361(3)	02-C1 1.372(3)
	02-C4 1.460(2)	03-C3 1.455(3)	02-C2 1.383(3)	02-C7 1.357(4)	02–C7 1.352(4)	02-C1 1.371(4)	02-C7 1.354(3)
	04-C18 1.343(2)	04-C18 1.344(2)	04-C21 1.359(2)	04-C23 1.384(4)	04–C23 1.377(4)	04-C29 1.363(3)	04-C27 1.356(3)
	04-C20 1.460(2)	04-C19 1.457(2)	04-C22 1.376(3)	04-C29 1.355(4)	04–C29 1.362(4)	04-C23 1.376(3)	04-C21 1.377(3)
C-C	C1-C2 1.491(2)	C1-C2 1.489(2)	C1-C8 1.485(3)	C7-C8 1.481(5)	C7-C8 1.483(4)	C7-C8 1.474(4)	C7-C8 1.482(3)
	C3-C4 1.529(2)	C3-C4 1.515(2)	C2-C7 1.377(3)	C1-C6 1.364(6)	C1-C6 1.375(6)	C1-C6 1.366(4)	C1-C6 1.378(3)
	C17-C18 1.491(2)	C17-C18 1.482(2)	C21-C28 1.483(3)	C29-C30 1.489(5)	C29-C30 1.486(5)	C29-C30 1.479(3)	C27-C28 1.478(3)
	C19-C20 1.511(3)	C19-C20 1.516(3)	C22-C27 1.377(3)	C23-C28 1.368(5)	C23-C28 1.381(5)	C23-C28 1.382(4)	C21-C26 1.381(3)
Coord. No.	10	10	9	9	9	9	10
Polyhedron	BCSAP ^a	SC ^b	MCSAP ^c	MCSAP	MCSAP	MCSAP	Cl ^d

^a BCSAP = bicapped square antiprism.
 ^b SC = sphenocorona.
 ^c MCSAP = monocapped square antiprism.
 ^d CI = cubicosahedron.

hydrogen bonding interaction is consistent with the small infrared $\Delta v_{\rm CN}$ value. There are also three inner sphere NO₃⁻ counter-ions bonded to the Nd(III) ion in an asymmetric, bidentate fashion. These atoms generate a 10-membered distorted bicapped square antiprism coordination polyhedron. The Nd-O(P) bond lengths, 2.4274(9) and 2.4136(9) Å, are typical of related coordination interactions involving neutral organophosphine oxide ligands [37-48,56,57]. It is noted that the shorter distance is associated with the monodentate (P)O-Nd interaction. The Nd-Nova-ring bond length, Nd–N1 2.655(1) Å, is significantly longer. Several intra-ligand bond lengths also show modifications with metal binding. For example, the P-O bond lengths, P1-O1 and P2-O3 bond lengths are identical, 1.497(1) Å, and they are longer than the free ligand bond length, 1.4865(8) Å. The ring C=N bond lengths in the complex, C2-N1 1.271(2) and C18-N2 1.264(2) Å are also both longer than the distance in the free ligand, 1.253(2) Å, and the bond lengthening is slightly greater for the ring that is involved in bidentate coordination to the Nd(III).

The unusual mixed monodentate/bidentate coordination condition found in $[Nd(2)_2(NO_3)_3(CH_3OH)]$ suggested that it might be possible to displace the coordinated, inner sphere CH₃OH molecule and produce a bis-bidentate coordination field with 2. Indeed, when the complex was dissolved in CH₃CN at 23 °C and the volatiles allowed to slowly evaporate, a white powder formed whose IR spectra (KBr) no longer showed evidence for CH₃OH. Furthermore, the spectrum showed bands at $v_{\rm CN} = 1637 \text{ cm}^{-1} (\Delta v_{\rm CN} = 22 \text{ cm}^{-1})$ and $v_{\rm PO} = 1158 \text{ cm}^{-1} (\Delta v_{\rm PO} = 31 \text{ cm}^{-1})$, and these coordination shifts are more in-line with bidentate ligand-metal interactions. It is noted that an identical IR spectra were obtained from solids isolated from 2:1 and 3:1 combinations of 2 with Nd(NO₃)₃ in CH₃CN solutions. The solid was crystallized from CH₃CN solution and single crystals suitable for X-ray diffraction analysis were obtained. A view of the molecule is shown in Fig. 6 and selected bond lengths are presented in Table 4. The complex contains two molecules of 2 both bonded to the Nd(III) ion in a bidentate PO,Noxa mode. The remaining inner sphere coordination positions are occupied by six O-atoms from three asymmetric, bidentate nitrate anions. It is noted that one of the two neutral ligand molecules appears to be more tightly bound than the other as indicated by the distances Nd-O1 2.3803(9) Å vs. Nd-O2 2.4189(9) Å and Nd-N1 2.660(1) Å vs. Nd-N2 2.691(1) Å. Both of the Nd-N distances are longer than the bidentate coordination interaction in the monodentate/bidentate structure described above: 2.655(1) Å. The changes in the intra-ligand bond lengths in the bis-bidentate complex upon coordination are similar to those observed in the monodentate/ bidentate complex: P1-O1 1.496(1), P2-O2 1.5015(9), C2-N1 1.275(2) and C18-N2 1.274(2) Å. Although the late lanthanide $Yb(NO_3)_3$ also forms a 2:1 complex with **2** in CH₃OH and CH₃CN, attempts to obtain X-ray quality crystals were unsuccessful. Therefore, it is not possible at this point to determine if a related monodentate/bidentate to bis-bidentate transformation takes place with the smaller lanthanide.

The 2:1 combinations of 3-5 with Nd(NO₃)₃·6H₂O and Yb(-NO₃)₃·6H₂O in methanol solutions led to formation of solid complexes following solvent evaporation. In general, CHN analytical data for the resulting powders matched best with 2:1 ligand/Ln compositions, but agreement in every instance was not within 3% relative to the assumed theoretical Ln(L)₂(NO₃)₃ compositions. This suggested that the solids contained labile inner and/or outer sphere water and/or methanol molecules, and this was confirmed by infrared spectra. The crude solid complexes were subsequently crystallized under different conditions in order to obtain single crystals suitable for X-ray diffraction analyses. Once more, the agreements of experimental CHN elemental analysis data with compositions deduced from the crystal structure analyses were unsatisfactory. The infrared spectra are complicated in the fingerprint region, but a band due to v_{PO} was identified in each complex and the Δv_{PO} values appear in a range 25–30 cm⁻¹. Overlapping bands in the region 1650–1550 cm⁻¹ precluded confident assignment of v_{CN} and therefore the data do not allow for a clear identification of ligand denticity.

The crystal structures for five complexes containing 3, 4 and 5 were determined. Four of these, [Yb(3)₂(NO₃)₃(H₂O)]·0.5(CH₃OH), $[Yb(4)_2(NO_3)_3(H_2O)]$, $[Nd(4)_2(NO_3)_3(H_2O)]$ and $[Yb(5)_2(NO_3)_3(-$ H₂O)] 0.5(CH₃CN), were found to have basically the same 2:1 ligand/metal composition differing only by the presence or absence of different outer sphere solvent molecules. Furthermore, the molecular structures are very similar. A view of one of the complexes, [Yb(3)₂(NO₃)₃(H₂O)]·0.5(CH₃OH) is shown in Fig. 7 and selected metrical parameters for each complex are summarized in Table 4. In each case, the lanthanide inner coordination sphere geometry approximates a mono-capped square antiprism generated by two oxygen atoms from two monodentate. (P)O bonded benzoxazole ligands, six oxygen atoms from three asymmetric. bidentate nitrate anions and one oxygen atom from an inner sphere water molecule. The two Ln–O(P) bond lengths in each complex are similar to each other within 0.03 Å, and, as expected, the Nd-O(P) bond lengths are longer than the Yb-O(P) bond lengths due primarily to the difference in lanthanide ionic radii [62]. In addition, the P=O bond length in each of the ligand



Fig. 6. Molecular structure and atom labeling scheme for $Nd(2)_2(NO_3)_3$. H-atoms omitted for clarity. Thermal ellipsoids are shown at the 20% level.



Fig. 7. Molecular structure and atom labeling scheme for $[Yb(3)_2(NO_3)_3(-H_2O)] \cdot 0.5MeOH$. Outer sphere MeOH and H-atoms, except on inner sphere water omitted for clarity. Thermal ellipsoids are shown at the 20% level.

fragments elongates relative to the free ligand upon coordination to the lanthanide ions while the remaining bond lengths show little change. It is noted that there are hydrogen bond interactions between the inner sphere water molecule H-atoms and the benzoxazole ring N-atom involving each monodentate ligand, and these orient the benzoxazole fragment N-atom toward the Ln(III) ion. The resulting O-H···N interactions are slightly more bent (range 161–173°) than observed with the complex containing **2** and MeOH, and the heavy-atom N···O separations fall in a range 2.709(4)–2.849(3) Å with the longer distances appearing in the complex containing ligand **5**.

The bis-monodentate PO-coordination conditions found with the complexes of **3–5** suggested that, like ligand **2**, it might be possible drive off the inner sphere water molecule and convert these complexes to bis-bidentate PO,N coordination complexes. Several different approaches to accomplish this conversion were examined. Based upon IR spectra, it appears that performing the syntheses of the complexes initially in hot MeOH or by heating the isolated bis-monodentate complexes in MeOH leads to replacement of the water, but MeOH probably remains O-bonded, in the inner coordination sphere. Attempts were made to expel the methanol by crystallization of the solids in hydrophilic and hydrophobic solvent combinations, but in only one case were X-ray crystallographic quality single crystals obtained: [Nd(3)₂(NO₃)₃]·3CHCl₃. A view of this molecule is shown in Fig. 8 and selected bond lengths are presented in Table 4. In parallel with the observations with ligand 2 in its Nd complex, the inner sphere water molecule in the complex $[Nd(3)_2(NO_3)_3(H_2O)]$, and likely MeOH in an intermediate composition, are displaced by the benzoxazine ring N-atom of both PO-bonded ligands. The two bidenate ligands and three bidentate nitrate groups generate a 10-coordinate cubicosahedron inner sphere geometry. The Nd-O(P) and Nd-N_{ring} bond lengths are similar to those observed in the $[Nd(2)_2(NO_3)_3]$ complex. The intraligand bond lengths for **3** in the bidentate condition are essentially identical to the bond lengths for monodentate **3** in $[Yb(3)_2(NO_3)_3(H_2O$] $0.5(CH_3OH)$ which suggests that the electronics in the ligand framework are not significantly perturbed by metal binding.

The results described here indicate that the inner sphere compositions and molecular structures of the coordination complexes formed by ligands of type I and J with Ln(III) cations are variable and dependent upon at least, the competing coordinating abilities of the ligands, the solvent molecules, H_2O , MeOH and MeCN, and



Fig. 8. Molecular structure and atom labeling scheme for $[Nd(3)_2(NO_3)_3]$ -3CHCl₃. Outer sphere CHCl₃ molecules and H-atoms omitted for clarity. Thermal ellipsoids are shown at the 20% level.

the counter-anions. This is not unexpected since many related observations have been reported in the lanthanide coordination chemistry literature [63], and similar behavior has been observed in our studies of ligands C-H bonded to Ln(III) cations [38-51,56–59]. A unique feature in the present study is that we have been able to isolate and structurally characterize complexes where the ligand reveals both its partial and full chelation potential in the solid state structures. A particularly relevant, parallel multifunctional phosphine oxide donor system involving dynamic chelation has been reported by Ziessel and coworkers [64]. By using a combination of X-ray crystallography, solution absorption and emission spectroscopy and computational analyses, the interactions of a potentially pentadentate bis(bipyridine) phosphine oxide ligand, PhP(O)[CH₂bipyr(CH₃)]₂, were thoroughly characterized, and the ligand denticity in solution was found to be dependent upon solvent and anion coordinating ability. In both systems it appears that hydrogen bonding between coordinated solvent and ligand also plays a role in stabilizing structures.

4. Conclusion

Unlike ligands of types **C**, **E** and **G**, ligands of types **I** and **J** probably hold little practical potential as solvent extraction reagents for f-block elements. However, their coordination chemistry is interesting and provides fundamental information about the outcome of competing interactions between various donor centers as well as additional examples of dynamic hemilabile interactions on Ln(III) cations. In the present examples, it is apparent that the phosphine oxide provides the stable ligand–metal interaction while the ring N-atom acts as the labile center in competition with solvent and anion donors. These initial results suggest that further studies of the solution phase ligand–metal interactions should be explored by detailed absorption and emission spectroscopies.

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Appendix A. Supplementary data

CCDC 740145 (**2**), 793390 (**3**), 793391 (**4**), 793392 (**5**), 740146, 740147, 793393, 793394, 793395, 793680, 793396 contain the supplementary crystallographic data for $[Nd(2)_2(NO_3)_3(CH_3OH)]$, $[Nd(2)_2(NO_3)_3]$, $[Yb(3)_2(NO_3)_3(H_2O)] \cdot 0.5(CH_3OH)$, $[Nd(3)_2(NO_3)_3] \cdot 3$ $(CHCl_3)$, $[Yb(4)_2(NO_3)_3(H_2O)]$, $[Nd(4)_2(NO_3)_3(H_2O)]$, $[Yb(5)_2(NO_3)_3$ $(H_2O)] \cdot 0.5(CH_3CN)$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2011.08.012.

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