Rare Earth Mixed Sandwich Complexes with Tetraalkylphospholide and Cyclooctatetraenide Ligands


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Graphical Abstract

Mixed Phospholide COT Sandwich Complexes

- Synthesis
- SC-XRD
- Multinuclear NMR
  \(^1\text{H}, \, ^{13}\text{C}, \, ^{31}\text{P}, \, ^{45}\text{Sc}, \, ^{89}\text{Y}\)
Highlights

• Mixed sandwich complexes with diamagnetic rare earths Sc, Y, La and Lu.
• Structures depend on metal ionic radius, and ligand steric and solubility.
• Metal–ligand coupling observed by solution $^{13}$C{¹H} and $^{31}$P{¹H} NMR spectroscopy.

Abstract

A series of rare earth (mono)phospholide mixed sandwich complexes of the general form [M(PC₄R₄)(COT)(THF)$_n$] (M = Sc, Y, La, Lu; R = Me, Et; COT = cyclooctatetraenide, {C₈H₈}²⁻; $n = 0$ to 2) have been isolated by the treatment of iodide precursors, [M(COT)(I)(THF)$_n$], (1M, M = Sc, Y, Lu, $n = 2$; M = La, $n = 3$) with potassium phospholide salts, [K(PC₄R₄)]$_n$ (R = Me, Et). The solid-state molecular structures and speciation of these sandwich complexes depends upon both the ionic radius of the rare earth metal, along with small steric and solubility differences which arise between the two per-alkylated phospholide ligands. The smaller {PC₄Me₄} ligand gave monomeric Lewis-base free [M(C₈H₈)(PC₄Me₄)] (2M, M = Sc, Lu) with smaller rare earths Sc(III) and Lu(III), but moving to larger ions Y(III) and La(III), the products were poorly soluble and could only be isolated as THF-adducts, [Y(C₈H₈)(PC₄Me₄)(THF)] (3) and [La(C₈H₈)(PC₄Me₄)(THF)$_2$] (4). The slightly increased steric demands of {PC₄Et₄} gave monomeric Lewis-base free complexes for Sc(III), Lu(III), and Y(III) in [M(C₈H₈)(PC₄Et₄)] (5M, M = Sc, Y, Lu), whereas for La(III) a dimeric complex was isolated, [La(C₈H₈)(µ-PC₄Et₄)]$_2$ (6). We also report the synthesis and molecular structures of 1Sc and 1Lu, as well as [LuI₃(THF)$_3$] (7) for the first time. All complexes were characterised by single crystal X-ray diffraction, multi-nuclear NMR, UV-Vis-NIR and ATR-IR spectroscopies in addition to elemental analysis.
1. Introduction

Cyclopentadienide (Cp, \{C_5H_5\}^–) and cyclooctatetraenide (COT, \{C_8H_8\}_2^2–) complexes are ubiquitous in rare-earth and actinide organometallic chemistry,[1-5] and have delivered landmark advances in metal-metal bonding[6-9], molecular magnetism[9-13], and small molecule activation[14-17] (Figure 1 A-D for some example complexes). Parent Cp and substituted derivatives, CpR, \{C_5R_5\}, also find extensive use as inert spectator ligands in catalysts due to their ability to saturate coordination spheres and support additional functionality as required[18-21]. Similarly, the tuneable steric demands of substituted derivatives CpR (and also COT derivatives, \{C_8R_8\}_2^2–) using a wide range of R groups allows for greater kinetic and thermodynamic stabilisation, and control over metal redox chemistry[22-29]. Both CpR and \{C_8R_8\}_2^2– ligand types have been used across the breadth of the periodic table to deliver isolable organometallic compounds with unique reactivities and properties[30-39].

![Diagram](https://doi.org/10.26434/chemrxiv-2024-j6gdf-v2)

**Figure 1.** A-D) Examples of some landmark rare earth and actinide CpR and \{C_8R_8\}_2^2– complexes. E) Schematic showing the differences in properties between \{C_5R_5\} and \{PC_4H_4\} anions. The e_2 HOMO level of the former is split into two non-degenerate HOMOs in the latter, one of which is concentrated on the P-atom.
Heterolide anions are analogous to the Cp anion but where one or more of the ring C-atoms has been replaced with a heteroatom (i.e. \{C_{5-n}R_{5-n}E_n\} where E is a heteroatom), such as phosphorus\(^{[40,41]}\). The chemistry of rare earth and actinide complexes supported by (mono)phospholide ligands, \{PC_4R_4\}, remains poorly developed with only 80 such structurally characterised examples in the CCDC by June 2024\(^{[42]}\), the vast majority of which has been undertaken by Nief, Mathey, Le Floch, and co-workers who contributed seminal results in the research area\(^{[42-51]}\). The chemistry of \{PC_4R_4\} ligands complements, but is divergent from, that of their Cp counterparts (Figure 1 E)\(^{[52]}\). For example, the heteroatom alters the donor and vibrational properties with implications for molecular magnetism such as with [Dy(Dtp)_2]^+ (Dtp = \{PC_4-2,5-tBu_2-3,4-Me_2\})\(^{[53]}\) and [Er(COT)(Dsp)] (Dsp = \{PC_4-2,5-TMS_2-3,4-Me_2\}; TMS = SiMe_3)\(^{[54]}\). Similarly, the electronic differences between Cp\(^R\) and \{PC_4R_4\} can significantly alter the redox properties of metal complexes.\(^{[29,55,56]}\)

Due to the barrier to entry in phospholide chemistry whereby ligand syntheses can be capricious and require multiple steps of air-free synthesis, much of the basic coordination chemistry such as their steric demands versus similarly substituted Cp\(^R\) ligands\(^{[57]}\), and the influence of oligomerisation on their crystallisation properties remains poorly defined. Herein we report the synthesis of heteroleptic COT phospholide complexes [M(COT)(TMP)] (2M, M = Sc, Lu), [Y(COT)(TMP)(THF)] (3), [La(COT)(TMP)(THF)_2] (4), [M(COT)(TEP)] (5M, M = Sc, Y, Lu), and dimeric [La(COT)(µ-TEP)]\(_2\) (6) by salt elimination between rare earth COT iodide complexes [M(COT)(I)(THF)_n] (1M, M = Sc, Y, Lu, n = 2; M = La, n = 3) and potassium salts of the alkylated phospholide ligands TMP (TMP = \{PC_4Me_4\}) and TEP (TEP = \{PC_4Et_4\}). All complexes were characterised by single crystal X-ray diffraction (SCXRD), multi-nuclear NMR (\(^1\)H, \(^{13}\)C, \(^{31}\)P, \(^{45}\)Sc, \(^{89}\)Y, as appropriate), UV-Vis-NIR and ATR-IR spectroscopies, and elemental analysis.
2. Experimental

2.1. General Methods

Unless otherwise described, all syntheses and manipulations were conducted under BOC PureShield argon (99.995%) with rigorous exclusion of oxygen and water using Schlenk line and glove box techniques in an MBraun Lab Star™. 3 Å molecular sieves were activated by heating for 8 hours at 300°C, 10⁻³ mbar. THF, n-hexane, and toluene were degassed by sparging and dried by passage through neutral alumina columns (INERT Corp.). THF was then degassed under vacuum and stored over 3 Å molecular sieves for 7 days before use. n-hexane and toluene were degassed under vacuum and stored over a K mirror and used immediately. C₆D₆ and C₄D₈O (Merck) were dried by refluxing over K metal, or CaH₂ in the case of C₅D₅N (Merck), for 4-5 days followed by vacuum transfer and storage in a J. Youngs valve appended vessel. [MI₃(THF)₃] (M = Sc, Lu) were prepared from metal powder (ca. 200 mesh) in analogy to other rare earth triiodide precursors[^58]. KTMP, KTEP and [La(COT)(I)(THF)₃] were prepared as described previously[^56,59,60]. Cyclooctatetraene (C₈H₈) was degassed and stored over 3 Å molecular sieves for 7 days prior to use, and K₂COT was prepared as an off-white powder by combining C₈H₈ with a slight excess of freshly cleaned K-metal in THF at room temperature for 18 hours, followed by filtration and removal of the volatiles under vacuum[^61]. Glass-fiber filter discs and PTFE-coated stirrer bars were stored in an oven (150°C) for at least 12 hours before use, and glassware was dried under vacuum (10⁻³ mbar) after strong heating with a butane flame. Solution phase UV-Vis-NIR spectra were collected at ambient temperature using a PerkinElmer Lambda 1050 UV-Vis-NIR spectrometer. Solutions were contained in a low volume (1 mL) screw-capped quartz cuvette with a 1 cm path length. ATR FT-IR spectra of microcrystalline samples were collected using a Bruker ALPHA II FT-IR spectrometer equipped with a Platinum ATR module with a diamond window. NMR spectroscopic data collection was performed on a Bruker Avance III
(400 MHz) or a Bruker Advance III HD (400 MHz). Elemental microanalyses (C/H/N) were carried out by Martin Jennings and Anne Davies at the University of Manchester.

2.2. Synthesis

[Sc(COT)(I)(THF)]$_2$ (1Sc). THF (30 mL) was added to a pre-cooled (−98°C) glass Schlenk vessel, equipped with a PTFE-coated stirrer bar, containing solid [ScI$_3$(THF)$_3$] (2.568 g, 4 mmol). Separately, THF (15 mL) was added to a glass Schlenk vessel, equipped with a PTFE-coated stirrer bar, containing solid K$_2$COT (0.729 g, 4 mmol) which immediately formed a dark orange solution which was then added dropwise to the [ScI$_3$(THF)$_3$] solution. The mixture was allowed to warm to room temperature and quickly became orange with a fine white precipitate, presumed to be KI. After stirring at room temperature overnight (16 hours), the solids were allowed to settle before filtration through a glass microfibre filter disc. Concentration of the clear orange supernatant to ca. 10 mL gave a large quantity of orange solids which were heated into solution and allowed to cool slowly to give large orange blocks of 1Sc. This mixture was stored at 5°C for 2 hours followed by −30°C for 16 hours to increase the yield. Crystals were isolated by decanting the supernatant followed by drying under vacuum (10$^{-3}$ mbar, 2 hours). A second crop was obtained in a similar fashion (combined yield = 1.363 g, 81.1%).

Elemental analysis on C$_{16}$H$_{24}$O$_2$ISc calc. (%): C = 45.73, H = 5.76, N = 0.00; found (%): C = 42.36, H = 5.40, N = 0.00.

$^1$H NMR (C$_6$D$_6$ and C$_5$D$_5$N 400.13 MHz, 298 K): δ = 6.72 (s, 8H, COT C), 3.49 (m, 8H, THF H), 1.41 (m, 8H, THF H).

$^{13}$C($^1$H) NMR (C$_6$D$_6$ and C$_5$D$_5$N, 100.62 MHz, 298 K): δ = 97.90 (s, COT C), 67.44 (s, THF C), 25.42 (s, THF C).

UV-vis-NIR (THF): $\lambda_{\text{max}}$ (cm$^{-1}$; ε) = A broad feature extends from ~400 nm (20,000 cm$^{-1}$) into the UV region, and beyond our spectral range.
FT-IR (ATR, microcrystalline) cm⁻¹ = 3,027 (vw), 2,970 (m), 2,951 (w), 2,892 (w), 1,874 (vw), 1,766 (vw), 1,637 (vw), 1,469 (w), 1,447 (w), 1,361 (vw), 1,342 (w), 1,313 (w), 1,295 (vw), 1,243 (w), 1,213 (vw), 1,174 (vw), 1,065 (vw), 1,036 (w), 1,011 (vs), 956 (vw), 927 (w), 906 (vs), 855 (vs), 787 (m), 775 (m), 758 (m), 715 (vs), 666 (vs), 617 (s), 600 (s), 575 (s), 567 (s), 559 (s), 551 (s), 530 (vs), 504 (s), 493 (s), 475 (m), 462 (s), 452 (m), 427 (m), 419 (m), 409 (m).

[Lu(COT)(I)(THF)]₂ (1Lu). The complex was prepared analogously to 1Sc above – [Lul₃(THF)]₃ (3.088 g, 4 mmol), K₂COT (0.729 g, 4 mmol). The dark brown solution gave 1Lu as colourless blocks over two crystalline crops (combined yield = 1.275 g, 58%).

Elemental analysis on C₁₆H₂₄O₂Lu calc. (%): C = 34.92, H = 4.40, N = 0.00; found (%): C = 33.94, H = 4.27, N = 0.00.

¹H NMR (C₆D₆ and C₅D₅N, 400.13 MHz, 298 K): δ = 6.63 (s, 8H, COT CH), 3.54 (m, 8H, THF–H), 1.43 (m, 8H, THF H).

¹³C{¹H} NMR (C₆D₆ and C₅D₅N, 100.62 MHz, 298 K): 94.52 (s, COT C), 67.81 (s, THF C), 25.79 (s, THF C).

UV-vis-NIR (THF): λmax (cm⁻¹; ε) = A broad feature extends from ~350 nm (28,000 cm⁻¹) into the UV region, and beyond our spectral range.

FT-IR (ATR, microcrystalline) cm⁻¹ = 3,019 (w), 2,970 (s), 2,955 (s), 2,927 (m), 2,894 (s), 1,870 (vw), 1,850 (vw), 1,745 (vw), 1,613 (vw), 1,482 (w), 1,469 (m), 1,445 (s), 1,344 (m), 1,311 (m), 1,297 (vw), 1,245 (w), 1,233 (vw), 1,182 (vw), 1,137 (vw), 1,093 (vw), 1,067 (vw), 1,007 (vs), 956 (vw), 927 (s), 917 (s), 900 (vs), 857 (vs), 775 (vs), 752 (s), 715 (vs), 668 (vs), 573 (s), 543 (s), 534 (m), 520 (s), 504 (m), 489 (m), 483 (m), 477 (w), 462 (m), 454 (m), 446 (w), 440 (w), 423 (w), 409 (w).
[Y(COT)(I)(THF)₂] (1Y). THF (40 mL) was added to a glass Rotaflu®-valve appended vessel, equipped with a PTFE-coated stirrer bar, containing Y⁰ metal filings (0.391 g, 4.4 mmol). The colourless suspension was cooled to (~98°C) and cyclooctatetraene (0.5 mL, 4.4 mmol) was added via a glass syringe followed by the dropwise addition of a THF solution of I² (0.558 g, 2.2 mmol). The mixture was allowed to warm to room temperature and quickly became opaque orange and then heated to 50 °C for 72 hours over which time the mixture turned light yellow with some fine grey solids. The solids were then allowed to settle before filtration at 50°C through a glass microfibre filter disc. Concentration of the clear orange supernatant to ca. 10 mL gave a large quantity of orange solids which were heated into solution and allowed to cool slowly to give large orange blocks of 2Y. This mixture was stored at 5°C for 2 hours followed by ~30°C for 16 hours to increase the yield. Crystals were isolated by decanting the supernatant followed by drying under vacuum (10⁻³ mbar, 2 hours). A second crop was obtained in a similar fashion (combined yield = 1.009 g, 49.4%).

Elemental analysis on C₁₆H₂₄O₂IY calc. (%): C = 41.40, H = 5.21, N = 0.00; found (%): C = 40.35, H = 5.14, N = 0.00.

¹H NMR (C₆D₆ and C₅D₅N, 400.13 MHz, 298 K): δ = 6.69 (s, 8H, COT CH), 3.55 (m, 8H, THF H), 1.43 (m, 8H, THF H).

¹³C{¹H} NMR (C₆D₆ and C₅D₅N, 100.62 MHz, 298 K): 94.52 (s, COT C), 67.81 (s, THF C), 25.79 (s, THF C).

UV-vis-NIR (THF): λ max (cm⁻¹; ε) = A broad feature extends from ~400 nm (24,000 cm⁻¹) into the UV region, and beyond our spectral range.

FT-IR (ATR, microcrystalline) cm⁻¹ = 405 (m) 413 (w) 419 (w) 432 (w) 446 (w) 464 (m) 479 (w) 489 (m) 504 (s) 516 (m) 532 (m) 538 (m) 551 (m) 575 (vs) 602 (s) 668 (vs) 711 (vs) 750 (s) 775 (s) 857 (vs) 896 (vs) 915 (s) 1009 (vs) 1096 (vw) 1176 (vw) 1245 (w) 1260 (vw) 1309 (w) 1344 (s) 1445 (w) 1469 (vw) 1482 (s) 1556 (m) 1615 (s) 1747 (vw) 1852 (vw) 2892 (vw) 2955 (vw) 2970 (vw) 3015 (vw).
[Sc(COT)(TMP)] (2Sc). THF (15 mL) was added to a pre-cooled (−98°C) stirring mixture of solid [Sc(COT)(I)(THF)2] (1Sc) (0.420 g, 1 mmol) and KTMP (0.178 g, 1 mmol) in a glass Schlenk vessel equipped with a PTFE-coated stirrer bar. The mixture was allowed to warm to room temperature and quickly became light-yellow with a fine white precipitate, presumed to be KI. After stirring at room temperature overnight (16 hours), the volatiles were removed under vacuum (10⁻³ mbar) which left a light-yellow powder. Toluene (20 mL) was added and briefly (< 1 min) refluxed with manual agitation to loosen solids from the vessel walls. The light-yellow solution and fine white solids were allowed to settle before filtration through a glass microfibre filter disc. Concentration of the bright yellow supernatant to ca. 3 mL gave a large quantity of colourless solids which were heated into solution and allowed to cool slowly to room temperature, stored at 5°C for 2 hours followed by −30°C for 16 hours to give large colourless blocks of 2Sc. A second crop was obtained in a similar fashion (combined yield = 0.150 g, 52%).

Elemental analysis on C₁₆H₂₀PSc calc. (%): C = 66.66, H = 6.99, N = 0.00; found (%): C = 66.81, H = 7.10, N = 0.00.

¹H NMR (C₆D₆, 400.13 MHz, 298 K): δ = 6.31 (s, 8H, COT C₉H₉), 1.90 (d, J₃HP = 10.0 Hz, 6H, TMP 2,5-(C(H₃)₂)₂), 1.67 (s, 6H, TMP 3,4-(C(H₃)₂)₂).

¹³C{¹H} NMR (C₆D₆, 100.62 MHz, 298 K): δ = 140.20 (d, JCP = 51.8 Hz, TMP 2,5-C(CH₃)₂), 131.56 (d, JCP = 4.4 Hz, TMP 3,4-C(CH₃)₂), 95.78 (s, COT C), 15.72 (d, JCP = 26.8 Hz, TMP 2,5-C(CH₃)₂), 13.79 (s, TMP 3,4-C(CH₃)₂).

³¹P{¹H} NMR (C₆D₆, 161.95 MHz, 298 K): δ = 95.67 (s, TMP P).

⁴⁵Sc NMR (C₆D₆, 97.15 MHz, 298 K): δ = 13.04 (s).

UV-vis-NIR (THF): λₘₐₓ (cm⁻¹; ε) = A broad feature extends from ~400 nm (24,000 cm⁻¹) into the UV region, and beyond our spectral range.
FT-IR (ATR, microcrystalline) cm$^{-1} = 3,044$ (vw), 2,994 (vw), 2,943 (m), 2,908 (s), 2,855 (s), 2,742 (vw), 2,721 (vw), 1,862 (w), 1,759 (m), 1,620 (vw), 1,492 (w), 1,469 (vw), 1,447 (s), 1,430 (m), 1,375 (vs), 1,313 (m), 1,260 (w), 1,093 (w), 1,015 (m), 898 (vs), 804 (vw), 773 (s), 754 (vs), 709 (vs), 569 (m), 553 (w), 522 (s), 495 (m), 483 (s), 464 (w).

$[\text{Lu(COT)(TMP)}] \ (2\text{Lu})$. The complex was prepared analogously to $2\text{Sc}$ above – $[\text{Lu(COT)(I)(THF)}_2] \ (0.550 \text{ g}, 1 \text{ mmol}), \text{KTMP} \ (0.178 \text{ g}, 1 \text{ mmol})$. The light-yellow solution gave $2\text{Lu}$ as colourless blocks over two crystalline crops (combined yield = 0.161 g, 38%). Elemental analysis on $\text{C}_{16}\text{H}_{20}\text{P}_{\text{Lu}}$ calc. (%): C = 45.94, H = 4.82, N = 0.00; found (%): C = 45.84, H = 4.80, N = 0.00.

$^1\text{H NMR (C}_6\text{D}_6, 400.13 \text{ MHz, 298 K)}: \delta = 6.24$ (s, 8H, COT CH), 1.96 (d, $^3J_{\text{HP}} = 9.9 \text{ Hz, } 6\text{H, TMP } 3,4\text{-CH}_3)$, 1.76 (s, 6H, TMP 2,5-CH$_3$).

$^{13}\text{C}^{[1}\text{H}] \text{ NMR (C}_6\text{D}_6, 100.62 \text{ MHz, 298 K)}: \delta = 141.68$ (d, $J_{\text{CP}} = 51.5 \text{ Hz, TMP } 2,5\text{-C(CH}_3)_2$), 132.79 (d, $J_{\text{CP}} = 4.2 \text{ Hz, TMP } 3,4\text{-C(CH}_3)_2$), 93.50 (s, COT C), 15.01 (d, $J_{\text{CP}} = 26.4 \text{ Hz, TMP } 2,5\text{-C(CH}_3)_2$), 13.50 (s, TMP 3,4-C(CH$_3$)$_2$).

$^{31}\text{P}^{[1}\text{H}] \text{ NMR (C}_6\text{D}_6, 161.95 \text{ MHz, 298 K)}: \delta = 88.36$ (s, TEP P).

UV-vis-NIR (THF): $\lambda_{\text{max}} \text{ (cm}^{-1}; \epsilon)$ = A broad feature extends from $\sim 380 \text{ nm (26,000 cm}^{-1})$ into the UV region, and beyond our spectral range.

FT-IR (ATR, microcrystalline) cm$^{-1} = 3,040$ (vw), 2,980 (vw), 2,908 (s), 2,855 (s), 2,738 (vw), 2,721 (vw), 2,692 (vw), 1,852 (vw), 1,747 (w), 1,603 (vw), 1,478 (w), 1,443 (m), 1,426 (m), 1,375 (vs), 1,305 (w), 1,260 (w), 1,217 (vw), 1,167 (vw), 1,147 (w), 1,095 (m), 1,054 (w), 1,013 (m), 954 (w), 892 (vs), 834 (w), 802 (m), 767 (m), 748 (s), 705 (vs), 625 (vs), 608 (s), 602 (s), 580 (s), 559 (m), 524 (vs), 481 (vs), 464 (s), 438 (s), 419 (s).
The complex was prepared analogously to 2Sc above – [Y(COT)(I)(THF)] (3). The light-yellow solution gave 3 as colourless blocks over a single crystalline crop from THF (yield = 0.075 g, 19%). Elemental analysis on C20H28OPY for 1 THF calc. (%): C = 59.41, H = 6.98, N = 0.00; for 0 THF calc. (%): C = 57.84, H = 6.07, N = 0.00; found (%): C = 57.72, H = 6.12, N = 0.00.

1H NMR (C6D6 and C4D8O, 400.13 MHz, 298 K): δ = 6.14 (d, JHY = 1.0 Hz, 8H, COT CH), 3.53 (s, THF H), 1.94 (d, 3JHP = 10.1 Hz, 6H, TMP 2,5-(CH3)2), 1.90 (s, 6H, TMP 3,4-(CH3)2), 1.42 (s, THF H).

13C{1H} NMR (C6D6 and C4D8O, 100.62 MHz, 298 K): δ = 141.14 (d, JCP = 45.4 Hz, TMP 2,5-(CH3)2), 132.44 (d, JCP = 3.2 Hz, TMP 3,4-(CH3)2), 98.15 (s, COT C), 15.62 (d, JCP = 26.4 Hz, TMP 2,5-(CH3)2), 14.01 (s, TMP 3,4-(CH3)2).

31P{1H} NMR (C6D6 and C4D8O, 161.95 MHz, 298 K): δ = 84.78 (d, JPY = 9.0 Hz, TMP P).

89Y-1H HSQC NMR (C6D6 and C4D8O, 19.60 MHz / 399.92 MHz, 298 K): δ = −155.43 / 5.60 (Y-COT-H).

UV-vis-NIR (THF): λmax (cm⁻¹; ε) = A broad feature extends from ~400 nm (24,000 cm⁻¹) into the UV region, and beyond our spectral range.

FT-IR (ATR, microcrystalline) cm⁻¹ = 3,043 (vw), 3,009 (vw), 2,955 (vw), 2,935 (w), 2,925 (w), 2,904 (w), 2,869 (w), 2,855 (w), 2,723 (vw), 1,846 (vw), 1,745 (vw), 1,599 (vw), 1,545 (vw), 1,469 (w), 1,449 (s), 1,424 (w), 1,377 (vs), 1,320 (vw), 1,261 (vw), 1,178 (vw), 1,147 (m), 1,097 (vw), 1,026 (w), 1,009 (m), 956 (w), 906 (vs), 892 (vs), 839 (m), 781 (m), 762 (w), 713 (vs), 625 (s), 606 (s), 592 (s), 578 (m), 567 (m), 557 (s), 549 (s), 538 (m), 530 (s), 510 (vs), 483 (vs), 464 (s), 454 (s), 442 (m), 430 (s), 417 (m), 407 (vs).

[La(COT)(TMP)(THF)]2 (4). The complex was prepared analogously to 2Sc above – [La(COT)(I)(THF)]3 (0.568 g, 1 mmol), KTMP (0.178 g, 1 mmol). The light-yellow solution gave 4 as colourless blocks over a single crystalline crop from THF (yield = 0.320 g, 61%).
Elemental analysis on $\text{C}_24\text{H}_{36}\text{O}_2\text{P}$La calc. (%): C = 54.76, H = 6.89, N = 0.00; found (%): C = 54.46, H = 6.94, N = 0.00.

$^1$H NMR (C$_6$D$_6$ and C$_5$D$_5$N, 400.13 MHz, 298 K): $\delta$ = 6.25 (s, 8H, COT $\text{CH}_2$), 3.51 (m, 8H, THF $\text{H}$), 2.09 (s, 6H, TMP 3,4-(CH$_3$)$_2$), 1.76 (d, $^3$J$_{HP}$ = 9.7 Hz, 6H, TMP 2,5-(CH$_3$)$_2$), 1.43 (m, 8H, THF $\text{H}$).

$^{13}$C{$^1$H} NMR (C$_6$D$_6$ and C$_5$D$_5$N, 100.62 MHz, 298 K): $\delta$ = 140.91 (d, $J_{CP}$ = 43.3 Hz, TMP 2,5-C(CH$_3$)$_2$), 135.95 (d, $J_{CP}$ = 2.7 Hz, TMP 3,4-C(CH$_3$)$_2$), 93.20 (s, COT C), 67.7 (s, THF), 25.74 (s, THF), 15.51 (d, $J_{CP}$ = 26.3 Hz, TMP 2,5-C(CH$_3$)$_2$), 13.50 (s, TMP 3,4-C(CH$_3$)$_2$).

$^{31}$P{$^1$H} NMR (C$_6$D$_6$ and C$_5$D$_5$N, 161.95 MHz, 298 K): $\delta$ = 94.61 (TMP $\text{P}$).

UV-vis-NIR (THF): $\lambda_{\text{max}}$ (cm$^{-1}$; $\varepsilon$) = A broad feature extends from ~400 nm (24,000 cm$^{-1}$) into the UV region, and beyond our spectral range.

FT-IR (ATR, microcrystalline) cm$^{-1}$ = 417 (m), 425 (m), 442 (m), 452 (m), 460 (m), 475 (s), 491 (m), 514 (s), 536 (m), 578 (s), 612 (s), 666 (vs), 697 (vs), 748 (m), 765 (w), 832 (vs), 865 (vs), 882 (vs), 894 (s), 904 (s), 915 (m), 927 (w), 956 (vw), 1,021 (vs), 1,034 (vs), 1,139 (w), 1,171 (w), 1,245 (vw), 1,293 (vw), 1,305 (vw), 1,336 (w), 1,361 (vw), 1,375 (w), 1,402 (w), 1,447 (s), 1,488 (vw), 2,713 (vw), 2,746 (vw), 2,853 (s), 2,879 (s), 2,904 (s), 2,923 (w), 2,949 (m), 2,959 (w), 3,021 (w), 1,719 (vw), 1,580 (vw), 1,825 (vw), 1,092 (vw).

$[\text{Sc(COT)(TEP)}]$ (5Sc). THF (15 mL) was added to a pre-cooled (−98°C) stirring mixture of solid $[\text{Sc(COT)(I)}(\text{THF})_2]$ (1Sc) (0.420 g, 1 mmol) and KTEP (0.234 g, 1 mmol) in a glass Schlenk vessel equipped with a PTFE-coated stirrer bar. The mixture was allowed to warm to room temperature and quickly became light-yellow with a fine white precipitate, presumed to be KI. After stirring at room temperature overnight (16 hours), the volatiles were removed under vacuum (10$^{-3}$ mbar) which left a light-yellow powder. Toluene (20 mL) was added and briefly (< 1 min) refluxed with manual agitation to loosen solids from the vessel walls. The light-yellow solution and fine white solids were allowed to settle before filtration through a
glass microfibre filter disc. Concentration of the bright yellow supernatant to ca. 2 mL gave a large quantity of colourless solids which were heated into solution and allowed to cool slowly to room temperature, stored at 5°C for 2 hours followed by −30°C for 16 hours to give large colourless blocks of 5Sc. Concentration of the supernatant to ca. 1 mL did not afford any further crops (yield = 0.176 g, 51%).

Elemental analysis on C_{20}H_{28}PSc calc. (%): C = 69.75, H = 8.20, N = 0.00; found (%): C = 69.20, H = 8.09, N = 0.00.

{\textsuperscript{1}}H NMR (C_{6}D_{6}, 400.13 MHz, 298 K): δ = 6.30 (s, 8H, COT CH), 2.24 (m, 8H, TEP (CH_{2})_{4}), 1.21 (t, J_{HH} = 7.5 Hz, 6H, TEP 2,5-(CH_{3})_{2}), 0.83 (t, J_{HH} = 7.5 Hz, 6H, TEP 3,4-(CH_{3})_{2}).

{\textsuperscript{13}}C{\textsuperscript{1}}H NMR (C_{6}D_{6}, 100.62 MHz, 298 K): δ = 149.70 (d, J_{CP} = 53.6 Hz, TEP 2,5-(CH_{2}CH_{3})_{2}), 136.55 (d, J_{CP} = 5.0 Hz, TEP 3,4-(CH_{2}CH_{3})_{2}), 95.53 (s, COT C), 23.88 (d, J_{CP} = 20.6 Hz, TEP 2,5-(CH_{2}CH_{3})_{2}), 21.73 (s, TEP 2,5-(CH_{2}CH_{3})_{2}), 17.22 (d, J_{CP} = 13.0 Hz, TEP 3,4-(CH_{2}CH_{3})_{2}), 15.93 (s, TEP 3,4-(CH_{2}CH_{3})_{2}).

{\textsuperscript{31}}P{\textsuperscript{1}}H NMR (C_{6}D_{6}, 161.95 MHz, 298 K): δ = 88.49 (s, TEP P).

{\textsuperscript{45}}Sc NMR (C_{6}D_{6}, 97.15 MHz, 298 K): δ = −18.15 (s).

UV-vis-NIR (THF): \lambda_{\text{max}} (cm^{-1}; \varepsilon) = A broad feature extends from ~400 nm (24,000 cm^{-1}) into the UV region, and beyond our spectral range.

FT-IR (ATR, microcrystalline) cm\(^{-1}\) = 2,959 (vs), 2,927 (s), 2,869 (s), 1,864 (vw), 1,761 (w), 1,622 (vw), 1,492 (vw), 1,469 (m), 1,451 (s), 1,432 (m), 1,404 (vw), 1,389 (vw), 1,371 (s), 1,311 (m), 1,264 (w), 1,149 (vw), 1,112 (w), 1,089 (m), 1,054 (s), 1,007 (vw), 974 (vw), 962 (vw), 898 (vs), 843 (vw), 814 (w), 781 (s), 754 (vs), 711 (vs), 631 (m), 617 (w), 600 (w), 573 (s), 555 (w), 536 (m), 524 (m), 491 (s), 462 (m), 440 (vs), 419 (vs).

[Y(COT)(TEP)] (5Y). The complex was prepared analogously to 5Sc above – [Y(COT)(I)(THF)\(_2\)] (0.464 g, 1 mmol), KTEP (0.235 g, 1 mmol). The light-yellow solution gave 5Y as colourless blocks over a single crystalline crop (yield = 0.212 g, 55%).
Elemental analysis on C<sub>20</sub>H<sub>28</sub>PY calc. (%): C = 61.86, H = 7.27, N = 0.00; found (%): C = 61.13, H = 6.96, N = 0.00.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub> and C<sub>5</sub>D<sub>5</sub>N, 400.13 MHz, 298 K): δ = 6.14 (s, 8H, COT C<sub>2</sub>H<sub>2</sub>), 2.48 (q, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 4H, TEP 2,5-(CH<sub>2</sub>)<sub>2</sub>), 2.18 (m, 4H, TEP 3,4-(CH<sub>2</sub>)<sub>2</sub>), 1.11 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 6H, TEP 2,5-(CH<sub>2</sub>)<sub>2</sub>), 1.04 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 6H, TEP 3,4-(CH<sub>2</sub>)<sub>2</sub>).

<sup>13</sup>C{'H} NMR (C<sub>6</sub>D<sub>6</sub> and C<sub>5</sub>D<sub>5</sub>N, 100.62 MHz, 298 K): δ = 150.54 (dd, J<sub>CP</sub> = 48.4 Hz, J<sub>CY</sub> = 1.0 Hz, TEP 2,5-O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 137.63 (d, J<sub>CP</sub> = 4.0 Hz, TEP 3,4-O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 93.90 (d, J<sub>CY</sub> = 2.6 Hz, COT C<sub>2</sub>), 24.13 (d, J<sub>CP</sub> = 21.1 Hz, TEP 2,5-(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 21.93 (s, TEP 3,4-(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 18.19 (d, J<sub>CP</sub> = 11.7 Hz, TEP 3,4-(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 16.29 (s, TEP 3,4-(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>).

<sup>31</sup>P{'H} NMR (C<sub>6</sub>D<sub>6</sub> and C<sub>5</sub>D<sub>5</sub>N, 161.95 MHz, 298 K): δ = 82.28 (m, TEP P).

<sup>89</sup>Y-'H HSQC NMR (C<sub>6</sub>D<sub>6</sub> and C<sub>5</sub>D<sub>5</sub>N, 19.60 MHz / 399.92 MHz, 298 K): δ = −91.39 / 6.29 (Y-COT-H).

UV-vis-NIR (THF): λ<sub>max</sub> (cm<sup>−1</sup>; ε) = A broad feature extends from ~400 nm (24,000 cm<sup>−1</sup>) into the UV region, and beyond our spectral range.

FT-IR (ATR, microcrystalline) cm<sup>−1</sup> = 3,033 (vs), 2,962 (vw), 2,925 (vw), 2,867 (w), 1,867 (vs), 1,753 (vs), 1,611 (vs), 1,465 (m), 1,451 (vw), 1,432 (m), 1,398 (s), 1,371 (vw), 1,311 (w), 1,262 (s), 1,229 (vs), 1,149 (s), 1,097 (m), 1,087 (m), 1,054 (vw), 1,019 (s), 1,013 (s), 1,005 (s), 958 (vs), 892 (vw), 839 (s), 812 (s), 771 (s), 746 (vw), 705 (vw), 629 (w), 617 (w), 606 (w), 580 (m), 567 (w), 547 (m), 530 (w), 508 (m), 485 (w), 475 (w), 462 (m), 432 (vw), 415 (vw).

[Lu(COT)(TEP)] (5Lu). The complex was prepared analogously to 5Sc above – [Lu(COT)(I)(THF)]<sub>2</sub> (0.550 g, 1 mmol), KTEP (0.235 g, 1 mmol). The light-yellow solution gave 5Lu as colourless blocks over a single crystalline crop (yield = 0.277 g, 58%).

Elemental analysis on C<sub>20</sub>H<sub>28</sub>PLu calc. (%): C = 50.64, H = 5.95, N = 0.00; found (%): C = 50.89, H = 5.77, N = 0.00.
$^1$H NMR (C$_6$D$_6$, 400.13 MHz, 298 K): $\delta = 6.24$ (s, 8H, COT CH$_2$), 2.34 (dq, $^3$J$_{HP}$ = 8.8 Hz, $^3$J$_{HH}$ = 7.5 Hz, 4H, TEP 2,5-(CH$_3$)$_2$), 2.19 (q, $^3$J$_{HH}$ = 7.6 Hz, 4H, TEP 3,4-(CH$_3$)$_2$), 1.19 (t, $^3$J$_{HH}$ = 7.5 Hz, 6H, TEP 2,5-(CH$_3$)$_2$), 0.85 (t, $^3$J$_{HH}$ = 7.5 Hz, 6H, TEP 3,4-(CH$_3$)$_2$).

$^{13}$C($^1$H) NMR (C$_6$D$_6$, 100.62 MHz, 298 K): $\delta =$ 151.43 (d, $J_{CP}$ = 53.6 Hz, TEP 2,5-CH(CH$_2$CH$_3$)$_2$), 136.55 (d, $J_{CP}$ = 5.0 Hz, TEP 3,4-CH(CH$_2$CH$_3$)$_2$), 95.53 (s, COT C), 23.88 (d, $J_{CP}$ = 20.6 Hz, TEP 2,5-(CH$_2$CH$_3$)$_2$), 21.73 (s, TEP 2,5-(CH$_2$CH$_3$)$_2$), 17.22 (s, TEP 2,5-(CH$_2$CH$_3$)$_2$), 15.82 (s, TEP 3,4-(CH$_2$CH$_3$)$_2$).

$^{31}$P($^1$H) NMR (C$_6$D$_6$, 161.95 MHz, 298 K): $\delta =$ 81.36 (s, TEP P).

UV-vis-NIR (THF): $\lambda_{max}$ (cm$^{-1}$; $\varepsilon$) = A broad feature extends from ~380 nm (26,000 cm$^{-1}$) into the UV region, and beyond our spectral range.

FT-IR (ATR, microcrystalline) cm$^{-1}$ = 2,959 (vs), 2,925 (s), 2,867 (s), 2,842 (w), 2,803 (vw), 1,856 (vw), 1,751 (w), 1,613 (vw), 1,467 (m), 1,449 (vs), 1,432 (m), 1,398 (vw), 1,371 (vs), 1,311 (m), 1,262 (w), 1,149 (vw), 1,097 (w), 1,085 (w), 1,071 (vw), 1,054 (s), 1,003 (vw), 960 (vw), 892 (vs), 839 (vw), 812 (vw), 771 (w), 748 (s), 707 (vs), 619 (m), 612 (m), 567 (s), 543 (w), 528 (m), 510 (w), 489 (s), 464 (m), 446 (m), 434 (vs), 419 (s), 411 (s).

[La(COT)(µ-TEP)]$_2$ (6). The complex was prepared analogously to 5Sc above – [La(COT)(I)(THF)$_3$] (0.293 g, 0.5 mmol),$^{[62]}$ KTEP (0.117 g, 0.5 mmol). The light-yellow solution gave 6 as light-yellow blocks over a single crystalline crop and a single crop (yield = 0.0248 g, 6%).

Elemental analysis on C$_{40}$H$_{56}$P$_2$La$_2$ calc. (%): C = 54.80, H = 6.44, N = 0.00; found (%): C = 52.56, H = 6.44, N = 0.00.

$^1$H NMR (C$_6$D$_6$ and C$_8$D$_8$N, 400.13 MHz, 298 K): $\delta = 6.31$ (s, 8H, COT CH$_2$), 2.63 (dq, $^3$J$_{HP}$ = 15.1 Hz, $^3$J$_{HH}$ = 7.4 Hz, 4H, TEP 2,5-(CH$_3$)$_2$), 2.44 (m, 2H, TEP 3,4-(CH$_3$)$_2$), 2.20 (m, 2H, TEP 3,4-(CH$_3$)$_2$), 1.16 (t, $^3$J$_{HH}$ = 7.4 Hz, 6H, TEP 2,5-(CH$_3$)$_2$), 1.11 (t, $^3$J$_{HH}$ = 7.5 Hz, 6H, TEP 3,4-(CH$_3$)$_2$).
$^{13}$C\textsuperscript{(1)}H NMR (C\textsubscript{6}D\textsubscript{6} and C\textsubscript{5}D\textsubscript{5}N, 100.62 MHz, 298 K): $\delta = 151.58$ (d, $J_{CP} = 45.0$ Hz, TEP 2,5-(CH\textsubscript{2}CH\textsubscript{3})\textsubscript{2}), 136.55 (d, $J_{CP} = 5.0$ Hz, TEP 3,4-(CH\textsubscript{2}CH\textsubscript{3})\textsubscript{2}), 95.53 (s, COT C), 23.88 (d, $J_{CP} = 20.6$ Hz, TEP 2,5-(CH\textsubscript{2}CH\textsubscript{3})\textsubscript{2}), 21.73 (s, TEP 2,5-(CH\textsubscript{2}CH\textsubscript{3})\textsubscript{2}), 95.53 (s, COT C), 23.88 (d, $J_{CP} = 20.6$ Hz, TEP 2,5-(CH\textsubscript{2}CH\textsubscript{3})\textsubscript{2}), 15.93 (s, TEP 3,4-(CH\textsubscript{2}CH\textsubscript{3})\textsubscript{2}).

$^{31}$P\textsuperscript{(1)}H NMR (C\textsubscript{6}D\textsubscript{6} and C\textsubscript{5}D\textsubscript{5}N, 161.95 MHz, 298 K): $\delta = 93.69$ (s, TEP P).

UV-vis-NIR (THF): $\lambda_{max}$ (cm\textsuperscript{-1}; $\varepsilon$) = A broad feature extends from ~500 nm (20,000 cm\textsuperscript{-1}) into the UV region, and beyond our spectral range. FT-IR (ATR, microcrystalline) cm\textsuperscript{-1} = 3,036 (s), 3,007 (s), 2,957 (vw), 2,925 (vw), 2,865 (w), 2,781 (m), 2,738 (s), 2,709 (s), 2,659 (s), 2,649 (s), 2,602 (vs), 2,160 (vs), 1,841 (vs), 1,735 (s), 1,585 (vs), 1,538 (vs), 1,496 (vs), 1,445 (vw), 1,393 (m), 1,369 (w), 1,307 (w), 1,262 (m), 1,254 (m), 1,149 (m), 1,124 (s), 1,093 (w), 1,052 (w), 939 (s), 890 (vw), 843 (m), 828 (m), 810 (s), 758 (m), 744 (m), 697 (vw), 617 (w), 592 (w), 567 (w), 538 (vw), 528 (vw), 510 (vw), 485 (w), 467 (vw), 436 (vw), 407 (vw).

$[\text{LuI}_3(\text{THF})_3]$ (7). THF (125 mL) was added to a pre-cooled (0°C) 250 mL J. Youngs appended round-bottomed flask, equipped with a PTFE-coated stirrer bar, containing Lu\textsuperscript{0} metal filings (5.000g, 28.6 mmol). Solid iodine (10.888, 42.9 mmol) was added in portions against a strong flow of argon to the colourless suspension. The brown mixture was allowed to warm to room temperature. After stirring at room temperature for 3 days the brown mixture was concentrated to ca. 30 mL and the supernatant was filtered. The remaining brown solids were washed once with hexane (30 mL) and dried under vacuum (10\textsuperscript{-3} mbar, 8 hours) at room temperature. The grey solids were purified by Soxhlet extraction in THF. The grey solution was concentrated to ca. 50 mL and Et2O (50 mL) followed by pentane (50 mL) was added. The grey suspension was filtered, and the solids dried under vacuum (10\textsuperscript{-3} mbar, 8 hours) yielding $[\text{LuI}_3(\text{THF})_3]$ as a grey solid (yield = 20.825 g, 94%).

Elemental analysis on C\textsubscript{12}H\textsubscript{24}O\textsubscript{3}I\textsubscript{3}Lu calc. (%): C = 18.67, H = 3.13, N = 0.00; found (%): C = 18.47, H = 3.11, N = 0.00.

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\[^1\text{H}\text{ NMR}\ (\text{C}_6\text{D}_6\text{ and } \text{C}_5\text{D}_5\text{N}, 400.13\text{ MHz, } 298\text{ K): } \delta = 3.51\ (m, 12\text{H, THF } H), 1.43\ (m, 12\text{H, THF } H).\]

\[^{13}\text{C}\{^1\text{H}\}\text{ NMR}\ (\text{C}_6\text{D}_6\text{ and } \text{C}_5\text{D}_5\text{N}, 100.62\text{ MHz, } 298\text{ K): } 67.45\ (s, \text{THF } C), 25.43\ (s, \text{THF } C).\]

\[\text{FT-IR (ATR, microcrystalline) cm}^{-1} = 2,988\ (m), 2,974\ (m), 2,953\ (m), 2,929\ (w), 2,900\ (s), 2,875\ (m), 2,828\ (vw), 1,484\ (vw), 1,445\ (s), 1,342\ (s), 1,295\ (vw), 1,245\ (m), 1,178\ (m), 1,040\ (s), 995\ (vs), 950\ (s), 910\ (vs), 826\ (vs), 721\ (s), 707\ (s), 674\ (vs), 602\ (m), 592\ (m), 575\ (vs), 549\ (w), 536\ (w), 526\ (w), 516\ (vw), 508\ (w), 493\ (vw), 475\ (vw), 458\ (w), 448\ (vw), 427\ (vw), 421\ (w), 403\ (vw).\]

3. Results and Discussion

3.1. Synthesis and Spectroscopic Characterisation

The preparation of targeted rare earth phospholide COT complexes first required the rare earth cyclooctatetraenide complexes [M(COT)(I)(THF)]\(_n\) (1M, M = Sc, Y, Lu, \(n = 2\)) which were prepared by analogy to previously-reported [M(COT)(I)(THF)]\(_n\) (M = La, Ce, Pr, \(n = 3\); M = Y, Nd, \(n = 2\); M = Sm, \(n = 1\)) from M\(^0\) (M = La, Y) metal filings,\[^{60,63,64}\] one equivalent of cyclooctatetraene and half an equivalent of iodine at elevated temperatures in THF over several days. The crystal structure of 1Y has been reported previously, and the metrical parameters are in agreement with our own data which we will use for discussion (see below).\[^{65}\] In the case of 1Lu, this reaction failed and only [LuI\(_3\)(THF)]\(_3\) (7) could be isolated, the structure of which is reported here for the first time (see Supporting Information).

Elemental microanalysis and \(^1\text{H}\text{ NMR spectroscopy suggest } 7\text{ does not readily undergo desolvation under vacuum (10}^{-3}\text{ mbar) at room temperature. Complexes 1Sc and 1Lu were instead synthesised from the reaction between molecular triiodides [MI}_3(\text{THF})_3] (M = Sc, Lu) and K\(_2\)COT (Scheme 1).\[^{60}\] Crystallisation of 1M complexes from THF gave large yellow blocks suitable for single crystal XRD in fair to excellent yields (49-81%). After drying under
vacuum (2 hours at 10−3 mbar) elemental microanalysis confirmed that these complexes do not undergo desolvation under the conditions described.


With 1M (M = Sc, Y, La, Lu) in hand, we turned our attention to the isolation of phospholide complexes. The addition of THF to a pre-cooled (~98°C) mixture of 1M and one equivalent of either KTMP (TMP = {PC₄Me₄}) or KTEP (TEP = {PC₄Et₄}) gave white suspensions and pale straw-coloured solutions upon warming to room temperature with stirring overnight (16 hours). The mixtures were reduced to dryness under vacuum (10−3 mbar). In the case of [M(COT)(TMP)] (2M, M = Sc, Lu), [M(COT)(TEP)] (5M, M = Sc, Y, Lu), and [La(COT)(µ-TEP)]₂ (6), toluene was added followed by a brief period at reflux (<1 minute). The supernatant was filtered at room temperature and concentrated under vacuum. Storage at low temperature (5°C followed by −30°C) gave complexes 2M, 5M, and 6 as colourless blocks suitable for single crystal XRD in fair yields (38-58%). In the case of [Y(COT)(TMP)(THF)] (3) and [La(COT)(TMP)(THF)]₂ (4), the white solids were found to be insoluble in common non-coordinating solvents (hexane, toluene, benzene) and were
instead crystallised from THF as adducts in poor (3, 18%) or good (4, 61%) yields (Scheme 1).

The \(^1\)H NMR spectra for 2–6 are characteristic of complexes with these ligand sets\[^{[51,66]}\]. The TMP 2,5-Me groups in 2Sc, 2Lu, 3, and 4 present as doublets (\(^3J_{HP} = 10\) Hz) spanning a narrow range of \(^1\)H shifts (\(\delta_H = 1.76–1.96\)), while the 3,4-Me singlets appear slightly upfield (\(\delta_H = 1.67–1.89\)). In complexes 5M (M = Sc, Y, Lu) and 6, the CH\(_3\) protons of the TEP 2,5-Et (\(\delta_H = 1.11–1.21\)) groups are somewhat downfield of the 3,4-Et groups (\(\delta_H = 0.83–1.11\)) and both sets give typical triplet splitting patterns (\(^3J_{HH}\) ca. 7.5 Hz). The corresponding CH\(_2\) \(^1\)H resonances are only well-resolved for 2Lu where the 3,4-Et CH\(_2\) groups appear as a quartet (\(\delta_H = 2.19; ^3J_{HH} = 7.6\) Hz) and the 2,5-Et CH\(_2\) displays additional coupling to the adjacent \(^{31}\)P and appears as a doublet of quartets (\(\delta_H = 2.34; ^3J_{HP} = 8.8\) Hz, \(^3J_{HH} = 7.6\) Hz). The CH\(_2\) groups for the remaining TEP complexes (5Sc, 5Y, 6) show more complex coupling patterns or broadened features which may arise due to aggregation processes in solution or unresolved long-range coupling to the metal centre (see Supporting Information). In complex 3, the COT \(^1\)H resonance appears as a doublet (\(\delta_H = 6.14; ^2J_{HY} = 1.0\) Hz) due to the presence of \(^{89}\)Y (\(I = \frac{1}{2}, 100\%\) natural abundance), while in all other complexes, including 5Y, the COT group appears as a singlet over a small range (\(\delta_H = 6.24–6.31\)). While the COT \(^1\)H peak shows no coupling to \(^{89}\)Y in 5Y, the \(^{13}\)C\{\(^1\)H\} NMR spectrum shows a doublet for the COT \(^{13}\)C environment (\(\delta_C = 93.90, ^1J_{CY} = 2.6\) Hz) which is almost identical to that of 3 (\(\delta_C = 98.15, ^1J_{CY} = 2.6\) Hz); conversely, only 5Y shows \(^{13}\)C–\(^{89}\)Y coupling to phospholide ring C-atoms, whereby the 2,5- positions appear as a doublet of doublets due to additional \(^{13}\)C–\(^{31}\)P coupling (\(\delta_H = 150.54; ^1J_{CP} = 48.4\) Hz, \(^1J_{CY} = 1.0\) Hz) – for further information on the \(^{13}\)C\{\(^1\)H\} NMR spectra of all complexes, see the Supporting Information. The phospholide ligands present a convenient spectroscopic tag through the \(^{31}\)P (\(I = \frac{1}{2}, 100\%\) nat. abund.) nucleus which is also highly sensitive to its local environment\[^{[67,68]}\]. The \(^{31}\)P\{\(^1\)H\} NMR spectrum of 3

\[\text{https://doi.org/10.26434/chemrxiv-2024-j6gdf-v2 \text{ORCID: https://orcid.org/0000-0002-4330-2548 Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0}]}\]
reveals $^{31}$P-$^{89}$Y coupling (doublet, $\delta_H = 84.78$; $^1J_{PY} = 9.0$ Hz); however, with $5Y$ a more complex feature is seen which resembles a broad triplet ($\delta_P = 82.28$), the cause of which is not currently understood as the $^{89}$Y NMR spectrum (see below) does not reveal signs of aggregation. In principle we also could observe M–$^{31}$P coupling to: $^{45}$Sc ($I = \frac{7}{2}$, 100% nat. abund.) in $2Sc$ and $5Sc$; $^{139}$La ($I = \frac{7}{2}$, >99% nat. abund.) in $4$ and $6$; or $^{175}$Lu ($I = \frac{7}{2}$, >97% nat. abund.) in $2Lu$ and $5Lu$. Despite the presence of these abundant spin-active metal centres, the $^{31}$P{¹H} NMR spectra for all complexes display a single resonance (i.e. do not show coupling to the metal centre), and span a reasonably narrow range ($\delta_P = 81.36$–95.67) with no clear trend between the chemical shift or structural parameters in the solid state (see Supporting Information). The $^{45}$Sc NMR spectra of $2Sc$ and $5Sc$ each reveal a single broad resonance at 13.04 ppm and −18.15 ppm respectively, and the $^{89}$Y-¹H HSQC spectra of $3$ and $5Y$ reveal $^{89}$Y chemical shifts of −155.43 and −91.39 ppm respectively, both arise from coupling to the COT ring protons.

3.2 Structural Characterisation

The solid-state structures of $1M$ (M = Sc, Y, Lu), $2M$ (M = Sc, Lu), $3$, $4$, $5M$ (M = Sc, Y, Lu), $6$, and $7$ were determined by single crystal X-ray diffraction (SC-XRD, additional crystallographic data are compiled in the Supporting Information). Note that throughout the following section ESDs are not given on distances and angles which involve ring centroids (C$_8$ or C$_4$P) as these are not refined positions.

Complex $1Sc$ crystallised in the non-centrosymmetric space group P$c$ with $Z'=2$ whereas $1Y$ and $1Lu$ crystallised in the centrosymmetric space group P2$_1$/n with $Z'=1$. The data for $1Y$ and $1Lu$ were collected at 200 K and 250 K respectively as they were found to undergo phase changes below ca. 150 to 200 K, which did not go to completion upon cooling to 100 K (the low temperature limit of our instrument). While this process was reversible in the case
of 1Y, reverting to a pure phase up warming to 300 K, in the case of 1Lu the phase change was irreversible with little to no change observe when warming from 100 K back to 300 K.

**Figure 2.** Molecular structure of $[M$(COT)(I)(THF)$_2$] 1M (M = Sc, Y, Lu). Ellipsoids set at 30% probability and H-atoms and disordered components have been removed for clarity (operations: X, Y, Z).

The structures of 1M (M = Sc, Y, Lu) are shown in Figure 2 and all feature an η$^8$-COT ring, two coordinating THF molecules and an iodide in a pseudo-tetrahedral arrangement which is similar to $[La$(COT)(I)(THF)$_3$], although the latter has three coordinating THF molecules$^{[62]}$. The M···C$_8$-centroid distances range from 1.646(12) Å to 1.834(12) Å and follow the expected trend based on Lewis acidity / trivalent ionic radius (6-coordinate: Sc = 0.745 Å; Lu = 0.861 Å; Y = 0.900 Å; La = 1.032 Å$^{[69]}$) and are similar to other $[M$(COT)(I)(donor)$_n$] complexes in the literature, accounting for differences in the ionic radius of the metal ion$^{[62-65,70-76]}$. It is interesting to note that while the M···C$_8$-centroid distance in 1Sc compares well to that of $[Sc$(COT)(Cl)(DME)] (1.600 Å), both are significantly longer than in dimeric $[Sc$_2$(C_8H_6-1,4-TMS)$_2$]_2(µ-Cl)$_2$(µ-THF)] (1.535 and 1.550 Å), possibly due to the larger number of Sc–anion contacts in the latter which reduces the charge density at Sc$^{[77]}$, though in the related complex, $[Sc$(C$_8$H$_8$)(µ-Cl)(THF)]$_2$, the same distance is 1.597 Å$^{[78]}$. The C$_8$-centroid···M···I angle remains essentially invariant across the 1M complexes$^{[60,69]}$. Selected bond lengths and angles for 1M are summarised in Table 1.
Table 1. Selected bond distances (Å) and angles (°) for 1M.

<table>
<thead>
<tr>
<th></th>
<th>M–I (Å)</th>
<th>M–O(1) (Å)</th>
<th>M–O(2) (Å)</th>
<th>M···C₈-centroid (Å)</th>
<th>C₈-centroid···M···I (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Sc</td>
<td>2.983(9)</td>
<td>2.23(2)</td>
<td>2.286(19)</td>
<td>1.646</td>
<td>130.1</td>
</tr>
<tr>
<td>1Lu</td>
<td>3.008(5)</td>
<td>2.330(11)</td>
<td>2.351(14)</td>
<td>1.748</td>
<td>132.2</td>
</tr>
<tr>
<td>1Y</td>
<td>3.0614(6)</td>
<td>2.35(2)</td>
<td>2.384(11)</td>
<td>1.834</td>
<td>130.4</td>
</tr>
</tbody>
</table>

The TMP complexes 2M (M = Sc, Lu), 3, 4 all crystallised in the centrosymmetric space group P2₁/c with Z' = 1 except for 4 (Z' = 2), and their molecular structures are shown in Figure 3 in the order of increasing metal ionic radius (Sc < Lu < Y < La). All four feature an η⁸-COT ring and an η⁵-TMP ring with the metal coordination spheres in 3 and 4 completed by one or two coordinated THF molecules respectively.

Figure 3. Molecular structures of [Sc(COT)(TMP)] (2Sc), [Lu(COT)(TMP)] (2Lu), [Y(COT)(TMP)(THF)] (3), and [La(COT)(TMP)(THF)₂] (4). Ellipsoids set at 50% probability,
and H-atoms and disordered components have been removed for clarity (operations: X, Y, Z).

Both the M···C₈-centroid distances in 2Sc (1.5031 Å) and 2Lu (1.628 Å), and the M···C₄Pcentroid distances (2.129 Å in 2Sc to 2.262 Å in 2Lu) follow the expected trend based on their respective 6-coordinate trivalent ionic radii (ΔM···C₈-centroid = 0.1249 Å; ΔM···C₄P-centroid = 0.133 Å; Δrad = 0.116 Å) and the C₈-centroid···M···C₄Pcentroid angles decrease from 174.14° in 2Sc to 172.219° in 2Lu[69]. The M···C₈-centroid distances in 3 and 4 increase significantly from 1.783 Å in 3 to 2.0748 Å in 4 as well as the M···C₄Pcentroid distances which increase from 2.395 Å in 3 to 2.6946 Å in 4 — though, again, these differences are broadly in line with the differences in their respective ionic radii (Δrad = 0.132)[69], with the remainder likely due to the difference in their formal coordination numbers. The C₈-centroid···M···C₄Pcentroid angles decrease from (2.395 Å in 3 to 2.6946 Å in 4). The greater changes in bond metrics between 3 and 4 can be attributed to the coordination of an additional molecule of THF in 4 compared to 3. Selected bond distances and angles for complexes 2M, 3 and 4 are summarised in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>M–P(Å)</th>
<th>M···C₄Pcentroid (Å)</th>
<th>M···C₈-centroid (Å)</th>
<th>C₄Pcentroid···M···C₈-centroid (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Sc</td>
<td>2.631(2)</td>
<td>2.129</td>
<td>1.5031</td>
<td>174.14</td>
</tr>
<tr>
<td>2Lu</td>
<td>2.735(8)</td>
<td>2.262</td>
<td>1.628</td>
<td>172.22</td>
</tr>
<tr>
<td>3</td>
<td>2.853(3)</td>
<td>2.395</td>
<td>1.783</td>
<td>144.38</td>
</tr>
<tr>
<td>4</td>
<td>3.0632(4)</td>
<td>2.6946</td>
<td>2.0748</td>
<td>135.32</td>
</tr>
</tbody>
</table>

Complexes 5Y and 5Lu crystallised in Pbcα with Z′ = 1, and 5Sc crystallised in P2₁/n with Z′ = 1 and an additional molecule of toluene – note that all three were crystallised from
toluene. Complex 6 crystallised as a centrosymmetric dimer ($Z' = 0.5$) in C2/c. The molecular structures of 5M (M = Sc, Lu, Y), and 6 are shown in **Figure 4**.

**Figure 4.** Molecular structures of [Sc(COT)(TMP)] (5Sc), [Lu(COT)(TEP)] (5Lu), [Y(COT)(TEP)] (5Y), and [La(COT)(µ-TEP)]$_2$ (6). Ellipsoids set at 50% probability, and H-atoms and disordered components have been removed for clarity (operations for 5M: X, Y, Z; operations for 6: X, Y, Z; 3/2–X, 1/2–Y, 1–Z).

The three 5M complexes along with 6 feature η$^8$-COT rings along with an η$^5$-TEP ring, while 6 presents an additional bond between the TEP P-atom lone pair on one {La(COT)(TEP)} unit to a second La metal centre (La–P = 3.1781(3) Å). This interaction is similar to the dimeric arsolide COT complex [Sm(COT)(µ-TMAs)]$_2$ (TMAs = {AsC$_4$Me$_4$})$^{66}$, and also the silole complex [La{(µ-COT)K(THF)$_2$}(µ-SiC$_4$-2,5-TMS-3,4-Ph)]$_2$$^{79}$, but contrasts other examples such as [Nd(COT)(TMP)(HMPA)] (HMPA = OP(NMe$_2$)$_3$), [Er(COT)(DSP)], and

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[Nd(COT)(DSP)(THF)] which are monomeric[51,54,66,80]. In 5Sc, two of the ethyl groups lie in the plane of the TEP ring, somewhat sterically shielding the P-atom, and the other two point away from the metal, whereas in 5Lu and 5Y three point away from the metal and one lies in the plane of the ring. Complex 6 is the outlier where three ethyl groups point away from the metal while the fourth points inwards, towards the La centre. The $M\cdots C_8$-centroid distances in 5M range from 1.4997 Å in 5Sc to 1.701 Å in 5Y, then 2.0031 Å in 6. The difference between 5Y and 6 is larger than the difference in their ionic radii, though 6 has a higher formal coordination number. The $M\cdots C_4$-centroid distances display a similar trend from 2.1480 Å in 5Sc to 2.3555 Å in 5Y, while the equivalent distance in 6 is elongated significantly (2.6328 Å). The $C_8$-centroid $\cdots M\cdots C_4$-centroid angles decrease from 174.01° in 5Sc to 164.49° in 5Y.[69] Selected distances and angles for 5M and 6 are summarised in Table 3.

Table 3. Selected bond distances (Å) and angles (°) for 5M and 6.

<table>
<thead>
<tr>
<th></th>
<th>$M\cdots P$(Å)</th>
<th>$M\cdots C_4$-centroid (Å)</th>
<th>$M\cdots C_8$-centroid (Å)</th>
<th>$C_4$-centroid $\cdots M\cdots C_8$-centroid (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Sc</td>
<td>2.6774(4)</td>
<td>2.1480</td>
<td>1.4997</td>
<td>174.01</td>
</tr>
<tr>
<td>5Lu</td>
<td>2.7640(7)</td>
<td>2.2820</td>
<td>1.641</td>
<td>168.11</td>
</tr>
<tr>
<td>5Y</td>
<td>2.8270(3)</td>
<td>2.3555</td>
<td>1.701</td>
<td>164.49</td>
</tr>
<tr>
<td>6</td>
<td>3.0523(5)</td>
<td>3.1781(3)</td>
<td>2.0031</td>
<td>144.76</td>
</tr>
</tbody>
</table>

$^A$ Bridging La–P distance.

The Sc(III) and Lu(III) complexes in the 2M and 5M series are both monomeric base-free sandwich complexes and so their structures allow a comparison between the steric differences between the TMP and TEP ligand sets – though we cannot account for differences in crystal packing forces. Upon comparing the $M\cdots P$ bond distances in the two Sc(III) complexes, we find an increase from 2.631(2) Å in 2Sc to 2.6774(4) Å in 5Sc, though
any change in the C₄P···Sc···C₈-centroid angle does not reach statistical significance, and so the M–P lengthening instead is a manifestation of the larger Sc···C₄P centroid distance in 5Sc (2.1480 Å) than in 2Sc (2.129 Å). That is to say, the ethyl groups in the TEP ligand appear to site the C₄P ring further from the metal, rather than simply inducing increased (or decreased) co-planarity of the two arene rings. Comparing the M–P distances in the two Lu(III) complexes, we find an increase from 2.735(8) Å in 2Lu to 2.7640(7) Å in 5Lu, which again is accompanied by an increase in the M···C₄P_centroid distance from 2.262 Å (2Lu) to 2.2820 Å (5Lu), but this time the complex becomes slightly more bent, with the C₄P_centroid···Lu···C₈-centroid angle decreasing from 172.22° in 2Lu to 168.11° in 5Lu.

Unlike the Sc(III) and Lu(III) 2M and 5M complexes above, the M–P distances in TMP complexes 3 (2.853(3) Å) and 4 (3.0632(4) Å) are longer than in 5Y (2.8270(3) Å) and 6 (3.0523(5) Å). This reflects the higher formal coordination numbers in 3 and 4 due to coordination of one or two THF moieties respectively. The increased M–P bond lengths are also reflected in the longer C₄P_centroid···M distances in 3 and 4 than 5Y and 6. The TEP complexes 5Y and 6 feature larger C₄P_centroid···M···C₈-centroid angles as the THF units force this angle open in 3 and 4 – though it is interesting that in 3, which features a single additional Lewis-basic unit coordinated to the metal, the angle (144.38°) is similar to that of 6 (144.76°) which also has just one additional Lewis-base bound to the metal.

Reflecting the dearth of phospholide chemistry in general, there are few structurally characterised rare earth complexes using either the TMP or TEP ligand sets with which to compare the M–P bond lengths. However, Tilley previously reported [Sc(TMP)₂(μ-Cl)₂Li(TMEDA)] which has Sc–P distances (2.694(2) and 2.718(2) Å) that are somewhat longer than in 2Sc, presumably as the second TMP ligand provides greater steric crowding than the COT ligand in 2Sc⁴. For the larger rare earths, the nearest comparisons are
[La(TMP)\textsubscript{2}(μ:η\textsuperscript{6}-C\textsubscript{7}H\textsubscript{7})\textsubscript{2}K(η\textsuperscript{6}-C\textsubscript{7}H\textsubscript{8})] (La–P = 3.0407(15) and 3.0112(12) Å)\textsuperscript{[81]}, and [Nd(COT)(TMP)(HMPA)] (Nd–P = 2.968(8) Å)\textsuperscript{[80]} which both compare well to 4 (3.0632(4) Å) and 6 (3.0523(5) Å) once differences in the ionic radii of La(III) (1.032 Å) and Nd(III) (0.983 Å; Δ = 0.049 Å) are accounted for\textsuperscript{[69]}. In the case of dimeric 6, the La–P\textsubscript{bridging} distance (3.1781(3) Å) is shorter than the equivalent distance in [La(μ-TMP)(AlMe\textsubscript{4}-κ\textsuperscript{2}Me,Me)]\textsubscript{2} (3.1962(3) Å)\textsuperscript{[50]}, though the latter has a higher formal coordination number. Accounting for the difference in the ionic radius of 8-coordinate La(III) (1.160 Å) vs the 6-coordinate value (1.032 Å), the difference in La–P\textsubscript{bridging} bond lengths (ΔLa–P = 0.0181(4) Å) is negligible. The La–P lengths in [La(Htp)\textsubscript{2}(μ-BH\textsubscript{4})]\textsubscript{2} (3.089(5) and 3.138(3) Å; Htp = {PC\textsubscript{4}-2,5-tBu\textsubscript{2}-3,4-H\textsubscript{2}}) are slightly longer than those in 4 and 6, likely a reflection of the steric crowding about the P-atoms induced by the bulky tBu groups.\textsuperscript{[82]}

It is interesting to note that only 6 was isolated as a dimer through coordination of the P-atom lone pair on one TEP ring to a second La(III) metal centre, whereas in the case of the TMP analogue, 4, the complex is monomeric but contains two THF molecules bound to the La(III) metal centre. In a similar fashion, complex 5Y is monomeric and free of Lewis basic co-ligands, while 3 features a THF molecule bound to the Y(III) metal centre. It is likely that the poor solubility of TMP complexes 3 and 4 in non-coordinating solvents is due to their existence as dimeric (or higher order) species in the solid-state, except in the presence of an excess of a Lewis base (THF) to produce solvated monomers. Conversely, the slightly increased steric bulk of TEP possibly hinders dimer formation somewhat, but it may also significantly increase the solubility of the complexes and so 5Y could be extracted into non-coordinating solvents and crystallised without the presence of additional Lewis base coordination. This increased bulk is clearly not sufficient to preclude dimer formation with La(III) in 6. That the M–P\textsubscript{bridging} distance in 6 is shorter than in [La(μ-TMP)(AlMe\textsubscript{4}-κ\textsuperscript{2}Me,Me)]\textsubscript{2} lends credence to the argument that the different behaviour of the TMP and TEP ligand

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systems likely derives from crystal packing and solubility differences, rather than notable differences in their steric demands, though this requires further investigation.

4. Conclusion

To summarise, we have described the synthesis and molecular structures of a series of crystalline heteroleptic rare earth phospholide COT sandwich complexes using Sc(III), Y(III), La(III), and Lu(III) and employing two different per-alkylated phospholide ligands: {PC₄Me₄} (TMP) and {PC₄Et₄} (TEP). In addition to their molecular structures, these complexes have been characterised by ATR-IR, UV-Vis-NIR, and multinuclear NMR spectroscopy (¹H, ¹³C, ³¹P, ⁴⁵Sc, ⁸⁹Y, as appropriate). The title complexes were isolated from salt elimination reactions between KTMP or KTEP salts, and monomeric [M(COT)(I)(THF)ₙ] precursors (1M; M = Sc, Y, Lu, n = 2; M = La, n = 3). The synthesis and molecular structures of 1Sc and 1Lu are reported here for the first time, and 1Y was only recently reported⁶⁵. During the course of this work, we have also determined the molecular structure of [LuI₃(THF)₃] (7) for the first time.

With the smaller rare earth ions Sc(III) and Lu(III), both TMP and TEP ligands gave monomeric sandwich complexes of the form [M(COT)(PC₄R₄)] (R = Me, 2M, M = Sc, Lu; or R = Et, 5M, M = Sc, Lu) when crystallised from toluene. With the larger Y(III) ion, the smaller TMP ligand gave a poorly soluble species which could only be extracted into and crystallised from THF and hence formed the Lewis base adduct [Y(COT)(TMP)(THF)] (3), presumably due to oligomerisation in the solid state in the absence of THF. In a similar fashion, the La(III) complex with TMP was isolated from THF as a bis-THF adduct [La(COT)(TMP)(THF)₂] (4). With the larger TEP ligand, a Y(III) complex was isolated free of THF coordination in monomeric [Y(COT)(TEP)] (5Y), whereas the La(III) analogue was found to crystallise as dimeric [La(COT)(µ-TEP)] (6). These differences can be attributed to small differences in
the steric profile of TMP vs TEP, though we suspect this is eclipsed by differences in their crystal packing and solubility profiles. With the basic coordination chemistry of these ligand sets on diamagnetic rare earths established, work in our laboratory to better understand their behaviour with actinide elements is ongoing.

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Author contributions: CRediT

CND: Investigation, data curation, formal analysis, visualisation, writing – original draft. DJO: Investigation. RWA: Investigation, formal analysis, methodology. GFSW: Data curation, formal analysis, validation. CAPG: Conceptualisation, formal analysis, methodology, project administration, supervision, writing – review and editing.

Declaration of competing interest

The authors declare no competing financial interest.

Supplementary Materials

The following CCDC references contain the supplementary crystal data for this article: 1Sc (2364920), 1Y (2364921), 1Lu (2364922), 2Sc (2364923), 2Lu (2364924), 3 (2364925), 4 (2364926), 5Sc (2364927), 5Y (2364928), 5Lu (2364929), 6 (2364930), and 7 (2364931).
These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Raw experimental data (NMR, ATR-IR, UV-Vis-NIR spectroscopy) can be found freely at DOI: 10.48420/26097415. {{Embargoed until publication}} The authors have cited additional references within the Supporting Information[83-93].

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