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Guo, Zhifang, Blair, Victoria L., Deacon, Glen B., and Junk, Peter C. (2022)
Europium is different: solvent and ligand effects on oxidation state outcomes and C-F activation in reactions between europium metal and Pentafluorophenylsilver.
Chemistry: a European journal, 28 (3) .

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<https://doi.org/10.1002/chem.202103865>

Europium is different: Solvent and ligand effects on oxidation state outcomes and C-F activation in reactions between europium metal and pentafluorophenylsilver

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Abstract

Unique outcomes have emerged from the redox transmetallation/ protolysis (RTP) reactions of europium metal with $[\text{Ag}(\text{C}_6\text{F}_5)(\text{py})]$ (py = pyridine) and pyrazoles (RR'pzH). In pyridine, a solvent not normally used for RTP reactions, the products were mainly Eu^{II} complexes, $[\text{Eu}(\text{RR}'\text{pz})_2(\text{py})_4]$ (RR'pz = 3,5-diphenylpyrazolate (Ph₂pz) **1**; 3-(2-thienyl)-5-trifluoromethylpyrazolate (ttfpz) **2**; 3-methyl-5-phenylpyrazolate (PhMepz) **3**). However, use of 3,5-di-tert-butylpyrazole (*t*Bu₂pzH) gave trivalent $[\text{Eu}(\textit{t}\text{Bu}_2\text{pz})_3(\text{py})_2]$ **4**, whereas the bulkier N,N'-bis(2,6-difluorophenyl)formamidine (DFFormH) gave divalent $[\text{Eu}(\text{DFForm})_2(\text{py})_3]$ **5**. In tetrahydrofuran (thf), the usual solvent for RTP reactions, C-F activation was observed for the first time with $[\text{Ag}(\text{C}_6\text{F}_5)(\text{py})]$ in such reactions. Thus trivalent $[\{\text{Eu}_2(\text{Ph}_2\text{pz})_4(\text{py})_4(\text{thf})_2(\mu\text{-F})_2\} \{\text{Eu}_2(\text{Ph}_2\text{pz})_4(\text{py})_2(\text{thf})_4(\mu\text{-F})_2\}]$ (**6**), $[\text{Eu}_2(\text{ttfpz})_4(\text{py})_2(\text{dme})_2(\mu\text{-F})_2]$ (**7**), $[\text{Eu}_2(\textit{t}\text{Bu}_2\text{pz})_4(\text{dme})_2(\mu\text{-F})_2]$ (**8**) were obtained from the appropriate pyrazoles, the last two after crystallization from 1,2-dimethoxyethane (dme). Surprisingly 3,5-dimethylpyrazole (Me₂pzH) gave the divalent cage $[\text{Eu}_6(\text{Me}_2\text{pz})_{10}(\text{thf})_6(\mu\text{-F})_2]$ (**9**). This has a compact ovoid core held together by bridging fluoride, thf, and pyrazolate ligands, the last including the rare $\mu_4\text{-}1\eta^5(\text{N}_2\text{C}_3): 2\eta^2(\text{N},\text{N}): 3\kappa(\text{N}): 4\kappa(\text{N}')$ pyrazolate binding mode. With the bulky N,N'-bis(2,6-diisopropylphenyl)formamidine (DippFormH), which often favours C-F activation in RTP reactions, neither oxidation to Eu^{III} nor C-F activation was observed and $[\text{Eu}(\text{DippForm})_2(\text{thf})_2]$ (**10**) was isolated. By contrast, Eu reacted with $\text{Bi}(\text{C}_6\text{F}_5)_3$ and Ph₂pzH or *t*Bu₂pzH in thf without C-F activation, to give $[\text{Eu}(\text{Ph}_2\text{pz})_2(\text{thf})_4]$ (**11**) and $[\text{Eu}(\textit{t}\text{Bu}_2\text{pz})_3(\text{thf})_2]$ (**12**) respectively, the oxidation state outcomes corresponding to that for use of $[\text{Ag}(\text{C}_6\text{F}_5)(\text{py})]$ in pyridine.

Keywords

Redox transmetallation/protolysis (RTP) reaction;

Europium(II and III) complexes;

C-F activation reactions;

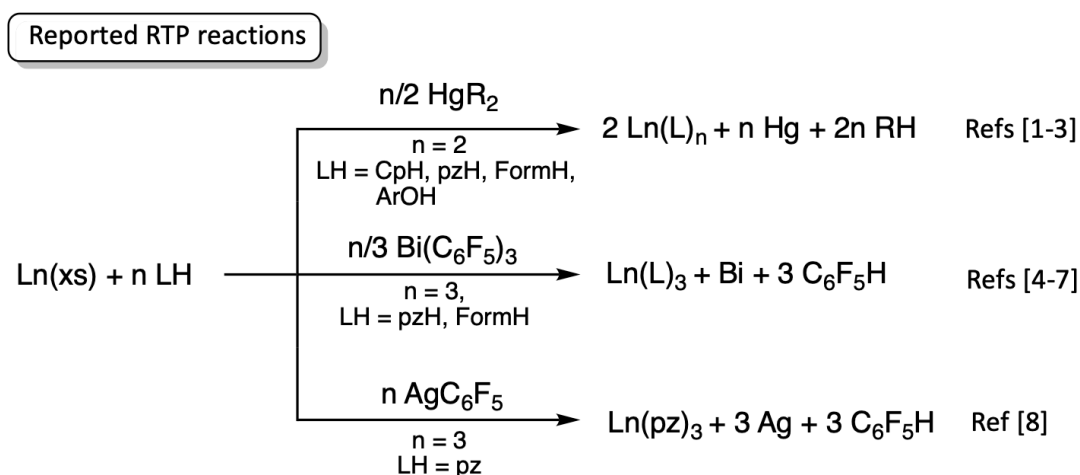
Pentafluorophenylsilver (AgC_6F_5);

Trispentafluorophenylbismuth ($\text{Bi}(\text{C}_6\text{F}_5)_3$);

Crystal structures.

Introduction

Redox transmetalation (RTP) reactions between free lanthanoid metals, diarylmercury compounds and weak protic acids (e.g. cyclopentadienes, phenols, pyrazoles, and formamidines etc.) are a relatively simple synthetic route to their highly reactive lanthanoid derivatives (Scheme 1).^[1-3] Of the reactants, only the lanthanoid metal is air/moisture sensitive and work-up is relatively simple. Although mercury can be recycled,^[3a] less toxic reagents would widen the appeal of the method. We have shown that $\text{Bi}(\text{C}_6\text{F}_5)_3$ can be used in the synthesis of lanthanoid pyrazolates^[4] and formamidinates (Scheme 1).^[5]



Scheme 1 Reported RTP reactions

However the organobismuth reagent is somewhat water-sensitive and is more difficult to prepare than $\text{Hg}(\text{C}_6\text{F}_5)_2$.^[3] Air stable, commercially available triphenylbismuth has been used in RTP reactions with alkaline earth metals,^[6,7] but has proven unreactive so far for the less electropositive lanthanoid metals.^[4] Another reagent, pentafluorophenylsilver has proved successful in the synthesis of lanthanoid pyrazolates ($\text{Ln}(\text{pz})_3$) (Scheme 1), but most heavier lanthanoid metals have to be activated by iodine.^[8] Moreover, this reagent was unsuccessful for the bulkier formamidinate ligands, and activation by iodine generally gave mixtures including formamidinato(iodido)lanthanoid(III) complexes.^[5] Silver N-heterocyclic carbenes

have been successfully used in redox transmetallation reactions to give lanthanoid(II) derivatives,^[9a, b] and silver tris(dialkylamido)imidophosphoranes to give Ce^{IV} species.^[9c] The attractions of AgC₆F₅ as a reagent have been enhanced by a simple new synthesis,^[8] but the compound is somewhat air/moisture sensitive and is very light-sensitive.

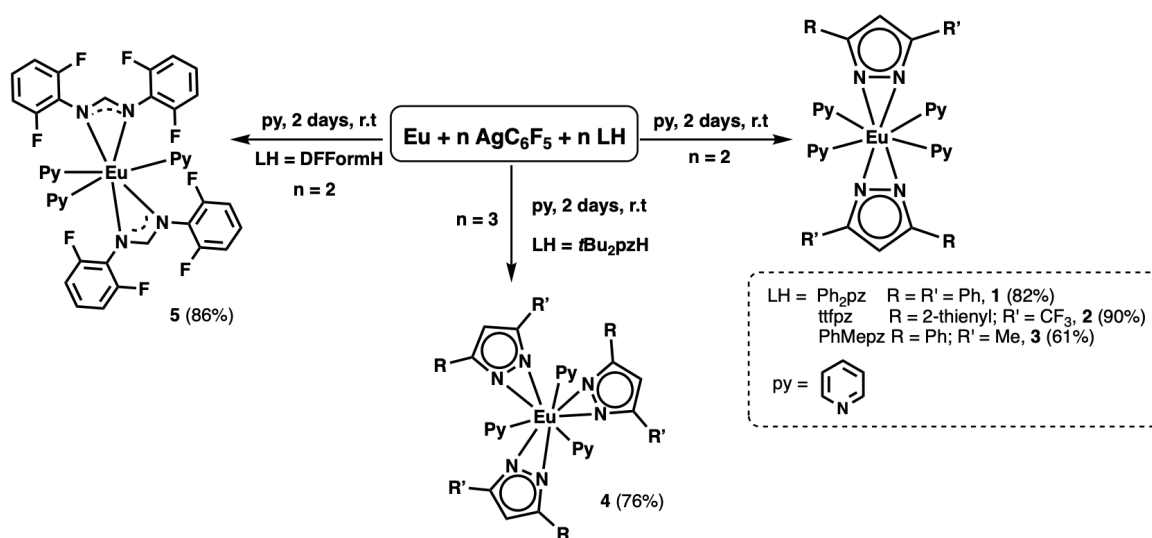
The reactivity of europium complexes and their applications in reduction chemistry, polymerization, luminescence, and as contrast agents for magnetic resonance imaging have been developed.^[10] We have not hitherto presented results for RTP reactions of europium metal with AgC₆F₅ and pyrazoles or formamidines, as their complexity and novelty required detailed evaluation. Indeed there has been little investigation of europium in RTP reactions with mercurials.^[3] We now report that these reactions give ligand dependent different oxidation state outcomes, and that, with the correct choice of solvent, the first examples of C-F activation in RTP reactions with AgC₆F₅ have been observed, leading to the first fluorido(pyrazolato)lanthanoid(III) complexes. C-F activation is of major current interest in rare earth chemistry and has been attracting increasing interest over four decades.^[11-12] Furthermore, unlike other Ln metals,^[5] Eu reacts cleanly with AgC₆F₅ and formamidines without the need for activation of the metal with iodine, unlike other Ln metals.^[5] Two comparable reactions with Bi(C₆F₅)₃ have also been carried out. The capacity of europium to stabilise divalent products is of particular interest as ytterbium gave only trivalent pyrazolates in reactions involving AgC₆F₅^[8] and Bi(C₆F₅)₃^[4] and only one divalent formamidinate utilising Bi(C₆F₅)₃.^[5]

Results and discussion

Synthesis of europium complexes by using AgC₆F₅ in pyridine (py)

Pyridine has been rarely used as a solvent for RTP reactions,^[3a] probably owing to concerns over possible free metal induced coupling reactions of pyridine,^[13] but its re-introduction has proved profitable. Thus, redox transmetallation/protolysis (RTP) reactions between an excess of Eu metal, equimolar amounts of [AgC₆F₅(py)] and pzH (Ph₂pzh, 3,5-diphenylpyrazole; ttfpzH, 3-(2-thienyl)-5-trifluoromethylpyrazole; PhMepzh, 3-methyl-5-phenylpyrazole; *t*Bu₂pzh, 3,5-di-*tert*-butylpyrazole) or DFFormH (N,N'-bis(2,6-difluorophenyl)formamidine) in pyridine at room temperature produced divalent europium complexes: [Eu(Ph₂pzh)₂(py)₄]·2py (**1**), [Eu(ttfpz)₂(py)₄] (**2**), [Eu(PhMepz)₂(py)₄] (**3**), [Eu(DFForm)₂(py)₃] (**5**) and trivalent [Eu(*t*Bu₂pz)₃(py)₂] (**4**) (Scheme 2). All reaction mixtures were monitored by ¹⁹F {¹H} NMR spectroscopy but due to the poor solubility of the complexes in py and the

paramagnetic nature of $\text{Eu}^{2+/3+}$, no useful spectra were obtained. Completion of the reactions was demonstrated by qualitative testing of an aliquot of the reaction mixture with HCl, when no AgCl precipitated, thereby indicating consumption of AgC_6F_5 . A silver mirror also formed. No divalent Eu pyrazolates or formamidates as pyridine complexes have been previously reported, but tris(3,5-di-tert-butylpyrazolato)lanthanoid(III) complexes $[\text{Ln}(\text{tBu}_2\text{pz})_3(\text{py})_2]$ ($\text{Ln} = \text{Y}, \text{Er}$) have been prepared by an RTP reaction of $\text{Hg}(\text{C}_6\text{F}_5)_2$ in toluene in the presence of a stoichiometric amount of pyridine.^[14a] Europium(II) complexes $[\text{Eu}(\text{Ph}_2\text{pz})_2(\text{dme})_2]$,^[3f, 14b] $[\text{Eu}(\text{tBu}_2\text{pz})_2(\text{dme})_2]$,^[3f] $[\text{Eu}(\text{DippForm})_2(\text{thf})_2] \cdot 2\text{thf}$,^[15] $[\text{Eu}(\text{DippForm})_2(\text{CH}_3\text{CN})_4] \cdot 2\text{thf}$ ^[16] $[\{\text{Eu}(\text{DFForm})_2(\text{CH}_3\text{CN})_2\}_2] \cdot 2\text{CH}_3\text{CN}$ ^[16] and trivalent $[\text{Eu}(\text{Ph}_2\text{pz})_3(\text{dme})_2] \cdot 2\text{dme}$ ^[17] and $[\text{Eu}(\text{tftpz})_3(\text{dme})_2] \cdot \text{dme}$ ^[18] have been previously prepared mainly by different methods, including redox transmetallation of thallium(I) pyrazolates or organotin pyrazolates, but no europium complexes of PhMepz and Me₂pz have been previously reported.



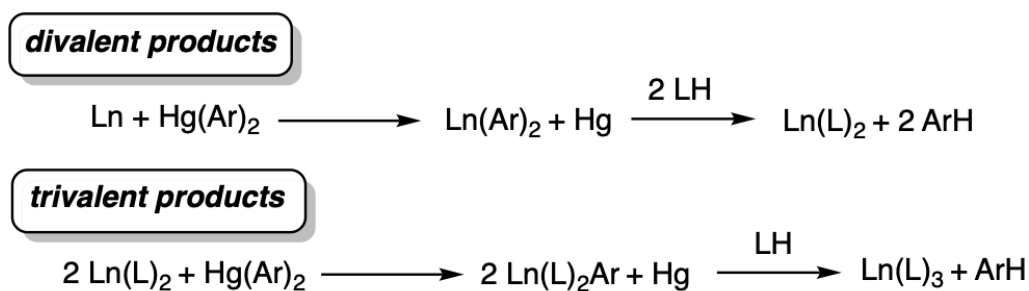
Scheme 2 Redox transmetallation/protolysis reactions of Eu, AgC_6F_5 and LH in py

Good to high yields (61-86%) of crystalline products were obtained after the filtrates were evaporated to half volume under vacuum. All the Eu complexes (**1-5**) crystallized as pyridine adducts and **1** also has two lattice pyridine molecules. Complexes **1-5** gave microanalyses for the bulk products as expected for the composition indicated by X-ray crystallography (below).

The surprise is the formation of trivalent **4** under the same conditions used for the preparations of **1-3**, though a pzH: AgC_6F_5 ratio of 1:1 is required for both classes (Scheme 2). We have earlier shown that RTP reactions of Eu, $\text{Hg}(\text{C}_6\text{F}_5)_2$, and carbazole or DippFormH form divalent products,^[3c, 15] but Eu metal, $\text{Hg}(\text{C}_6\text{F}_5)_2$ and cyclopentadiene in pyridine give $[\text{EuCp}_3(\text{py})]$.^[19]

An RTP reaction between Eu metal, *t*Bu₂pzH, and HgPh₂ in thf followed by crystallization from dme yields [Eu(*t*Bu₂pz)₂(dme)₂],^[3f] in contrast to the current behaviour with AgC₆F₅ in py.

There is considerable evidence that RTP reactions between Ln metals, diarylmercury compounds and proligands, proceed by redox transmetallation preceding protolysis (Scheme 3).^[3a]

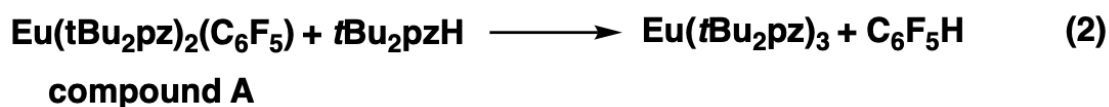
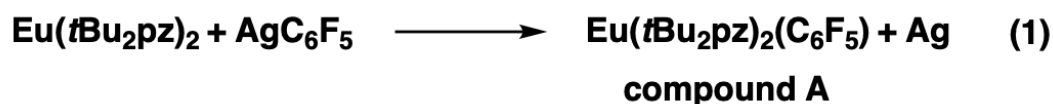


Scheme 3 Proposed path for RTP reactions of diarylmercurials

Europium metal is known to undergo redox transmetallation with Hg(C₆F₅)₂ in thf yielding [Eu(C₆F₅)₂(thf)₅],^[20] which readily undergoes protolysis reactions,^[21-22] and oxidation of YbCp₂ by Hg(C₆F₅)₂ analogous to the third step has been independently demonstrated^[23] as well as oxidation of [Sm(DippForm)₂] by Hg(CPh)₂ to [Sm(DippForm)₂(CPh)(thf)].^[24]

If there is a similar path for the reaction of Eu with AgC₆F₅ and pyrazoles, Ln(pz)₂ complexes would be obtained after two steps. Of the products at this stage, [Eu(*t*Bu₂pz)₂] would be expected to be the best reductant in the redox reaction [Scheme 4 eq.(1)] owing to the electron donating *tert*-butyl groups. Protolysis of the proposed pentafluorophenyleuropium(III) species (compound A) would yield Eu(*t*Bu₂pz)₃ [Scheme 4 eq.(2)]. Seemingly, the other divalent Ln(pz)₂ species are not sufficiently powerful reductants to react with AgC₆F₅. Qualitative tests indicate that the reaction of AgC₆F₅ with Eu metal is rapid, but considerable decomposition is observed (see Supplementary data).

Proposed formation of 5



Scheme 4 Proposed path for the formation of complex $\text{Eu}(t\text{Bu}_2\text{pz})_3$ 5

Molecular structures

Compounds **1-4** crystallize in the monoclinic space group $P2_1/c$. For **1-3**, the eight-coordinate europium atom is coordinated by two *transoid* or *trans* η^2 -pyrazolate ligands which occupy the axial positions (C(backbone)-Ln-C(backbone) 148° for **1** and 180° for **2, 3**) and four equatorial py ligands. In **4** Eu is eight coordinate with three η^2 - $t\text{Bu}_2\text{pz}$ ligands in a pseudo-meridional array (see C-Eu-C angles in **Figure 1**) and two *transoid* pyridine ligands (N7-Eu-N8 $144.99(7)^\circ$) (**Figure 1**). Single crystals of $[\text{Eu}(\text{DFForm})_2(\text{py})_3]$ (**5**) had unit cell parameters in agreement with recent reported X-ray data.^[25]

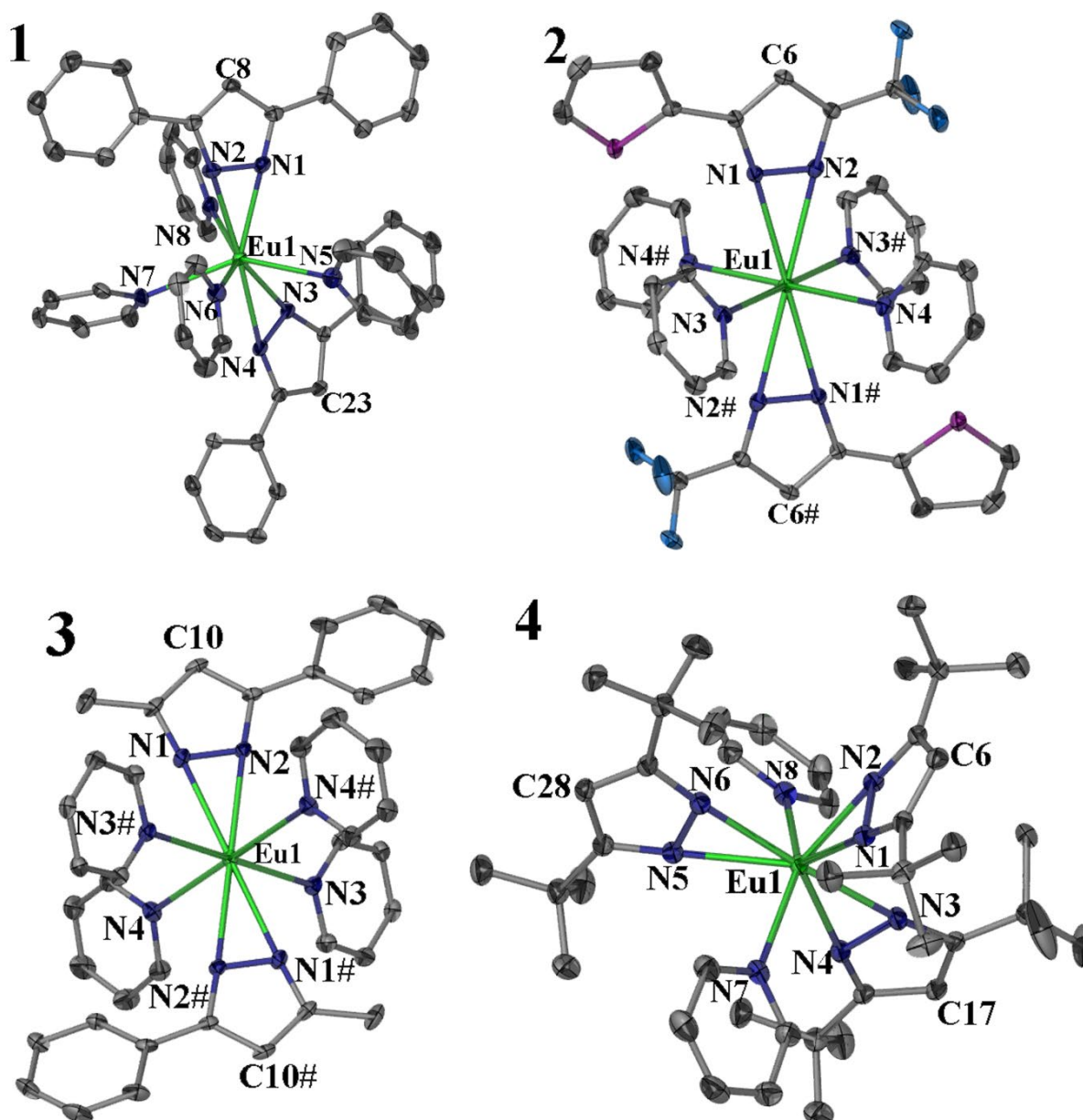
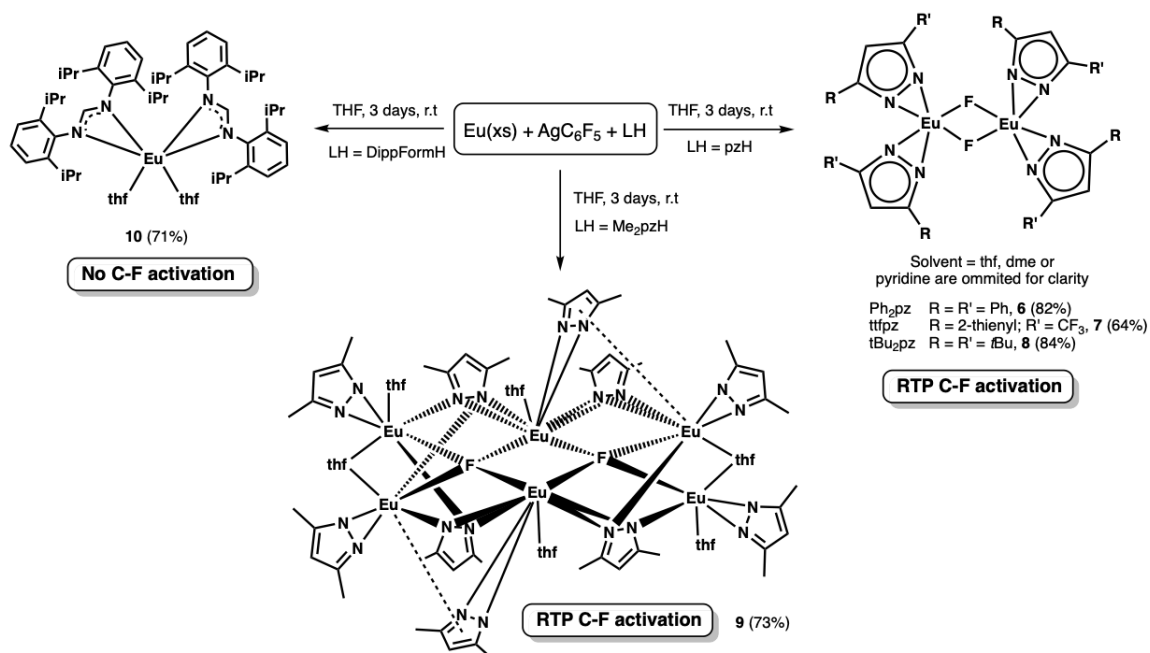


Figure 1. Molecular diagrams of [Eu(RR'pz)₂(py)₄] (Ph₂pZ, **1**; ttfpz, **2**; PhMepz, **3**) and [Eu(*t*Bu₂pZ)₃(py)₂] (**4**) with non-hydrogen atoms represented by 50% thermal ellipsoids. The lattice py molecules and hydrogen atoms have been omitted for clarity. **1** Eu-N(1) 2.555(4), Eu-N(2) 2.591(3), Eu-N(3) 2.538(3), Eu-N(4) 2.603(3), Eu-N(5) 2.705(4), Eu-N(6) 2.692(4), Eu-N(7) 2.722(4), Eu-N(8) 2.741(3), C8-Eu-C23 148.38; **2** Eu-N(1) 2.633(3), Eu-N(2) 2.661(3), Eu-N(3) 2.724(3), Eu-N(4) 2.724(3), C6-Eu-C6# 180, symmetry code: 1-X,1-Y,1-Z; **3** Eu-N(1) 2.6063(18), Eu-N(2) 2.6151(17), Eu-N(3) 2.7153(19), Eu-N(4) 2.7412(18), C10-Eu-C10# 180, symmetry code: 1-X,1-Y,1-Z; **4** Eu-N(1) 2.378(2), Eu-N(2) 2.384(2), Eu-N(3) 2.387(2), Eu-N(4) 2.430(2), Eu-N(5) 2.440(2), Eu-N(6) 2.368(2), Eu-N(7) 2.555(2), Eu-N(8) 2.588(2), C6-Eu-C17 105.783, C6-Eu-C28 107.499, C17-Eu-C28 146.485, N7-Eu-N8 144.99(7).

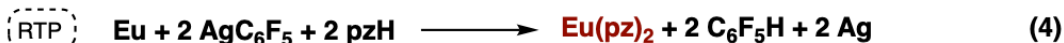
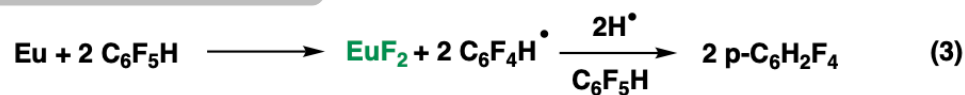
Synthesis of europium complexes by using AgC₆F₅ in thf — widespread C-F activation

RTP reactions of equimolar amounts of [AgC₆F₅(py)] and pZ (Ph₂pZH, ttfpZH, *t*Bu₂pZH and Me₂pZH) or DippFormH with an excess of Eu metal in thf at room temperature for three days yielded the fluoridoeuropium(III) complexes, [$\{Eu_2(Ph_2pZ)_4(py)_4(thf)_2(\mu-F)_2\} \{Eu_2(Ph_2pZ)_4(py)_2(thf)_4(\mu-F)_2\} \cdot 6thf$] (**6**), [Eu₂(ttfpz)₄(py)₂(dme)₂(μ-F)₂]·2dme (**7**), [Eu₂(*t*Bu₂pZ)₄(dme)₂(μ-F)₂] (**8**), and the Eu^{II} cage complex [Eu₆(Me₂pZ)₁₀(thf)₆(μ-F)₂] (**9**) (Scheme 5). Compounds **7** and **8** were obtained after work up with dme to obtain crystals. The corresponding reaction of DippFormH gave divalent [Eu(DippForm)₂(thf)₂]·2thf (**10**) and no C-F activation (Scheme 5). In contrast to the reactions in pyridine, trivalent products dominated, all arising from C-F activation. Although the formation of the divalent cage **9** involves C-F activation, the F:Eu ratio is 1:3 compared with 1:1 in the trivalent fluorides. The reaction mixtures were monitored by ¹⁹F {¹H} NMR spectroscopy (**Fig. S1-5**) showing consumption of [AgC₆F₅(py)] and formation of C₆F₅H on completion for complexes **6**, **8**, **9** and **10**. There was an additional resonance (**6**, **8**, **9** and **10**) near F-2,6 of C₆F₅H showing the formation of the by-product 1,2,4,5 tetrafluorobenzene caused by C-F activation of C₆F₅H by the Ln metal, as observed for Yb metal with accompanying YbF₂ formation^[26] (Preliminary results from the reaction of Eu metal, Hg(C₆F₅)₂, and C₅Ph₅H, analogous to the Yb metal/Hg(C₆F₅)₂/C₅Ph₄H₂ system, provide support for C-F activation of C₆F₅H by Eu metal).^[27] The spectra from either the reaction mixture for formation of **7** or dissolution of crystals showed no ¹⁹F resonance presumably owing to paramagnetic effects. The consumption of AgC₆F₅ was confirmed by qualitative tests. For the trivalent complexes **6-8** we consider that the excess Eu metal reacts with C₆F₅H to form EuF₂ [Scheme 6 eq. (3)], which reacts with Eu(pz)₂ formed by the RTP reaction [eq. (4)], to form [Eu(pz)F] [eq. (5)], which then undergoes an RTP reaction to form [Eu(pz)₂F]₂ [eq. (6)]. For the divalent complex **9**, the redistribution between Eu(Me₂pZ)₂ and EuF₂ involves a different stoichiometry [Scheme 6 eq. (7)] giving a stable cage (**9**), which is sufficiently bulky to be resistant to a further RTP reaction to Eu^{III}.



Scheme 5 C-F activation reactions of Eu with AgC₆F₅ and LH in thf

Proposed formation of **6-8** - trivalent



pzH = Ph₂pzH, ttfpzH, tBu₂pzH

Proposed formation of **9** - divalent



Scheme 6 Proposed path for C-F activation product formation from reactions of Eu with AgC₆F₅ and pyrazoles in thf

Reasonable yields (64-84%) of crystalline products were obtained after appropriate crystallization procedures (see experimental) but long times (two weeks to two months) and cooling were employed. Complex **6** crystallized from thf and complex **7** crystallized from dme have pyridine and either thf (**6**) or dme (**7**) coligands, even though the only source of pyridine is from the [AgC₆F₅(py)] reactant. Satisfactory microanalyses for **6-8** could not be obtained, but the Eu analyses were as expected for the single crystal composition.

[Eu(DippForm)₂(thf)₂]₂·2thf (**10**) has been previously isolated and structurally characterized.^[15] Complexes **9-10** gave microanalyses for the bulk products as expected for the composition indicated by X-ray crystallography. What is noteworthy about the Eu, AgC₆F₅, DippFormH reaction (Scheme 5) is the absence of sterically induced C-F activation giving [Eu(DippForm)₂F(thf)] and the trapped tetrafluorobenzene, *o*-HC₆F₄O(CH₂)₄N(Dipp)CH=N(Dipp), as observed in reactions of La, Ce, Nd, Sm, and Tm with Hg(C₆F₅)₂^[24] and DippFormH, and of Nd and Er with Bi(C₆F₅)₃ and DippFormH.^[5] In each case, metals both larger and smaller than Eu participate in sterically-induced C-F activation reactions. Thus, [Eu(DippForm)₂(thf)] is an insufficiently weak reductant to reduce Ag(C₆F₅) to give Eu(DippForm)₂(C₆F₅), the precursor of C-F activation by tetrafluorobenzene elimination. Divalent Eu is much more stable than divalent La, Ce, Nd, Sm, Er, and Tm.

Molecular structures

[{Eu₂(Ph₂pz)₄(py)₄(thf)₂(μ-F)₂} {Eu₂(Ph₂pz)₄(py)₂(thf)₄(μ-F)₂}]·6thf (1:1) (**6**) crystallized in the triclinic space group *P*-1, together with six lattice thf molecules. Eu1 and Eu1# are eight coordinate and are bonded in an η²-fashion by two *cis* pyrazolate ligands, two *transoid* py molecules (N1-Eu1-N6 158.80(19) °), one thf molecule, and two bridging fluorine atoms. Eu2 and Eu2# are eight coordinate and are bonded in an η²-fashion by two *cis* pyrazolate ligands, two *cis* thf molecules (O2-Eu2-O3 87.43(17) °), one py molecule and two bridging fluorine atoms (**Figure 2**). The average Eu-F bond length is 2.303 Å, which is similar to the reported Eu-F bond length 2.294 Å in [Eu₂(edta)₂F₂(H₂O)].^[28] The average Eu-N (pyrazolate ligands) bond length is Eu-N 2.479 Å, and the Eu-N (py) bond length (2.567 Å) is longer than Eu-N (pyrazolate ligands), consistent with the difference in charge.

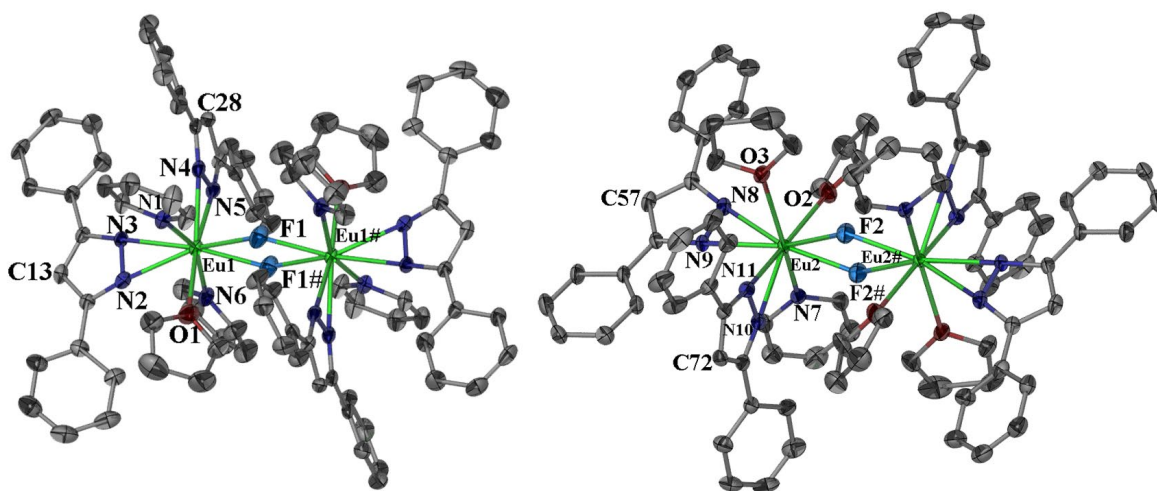


Figure 2. Molecular diagram of [$\{\text{Eu}_2(\text{Ph}_2\text{pz})_4(\text{py})_2(\text{thf})_2(\mu\text{-F})_2\} \{\text{Eu}_2(\text{Ph}_2\text{pz})_4(\text{py})_2(\text{thf})_2(\mu\text{-F})_2\}$]-6thf (**6**) without hydrogen atoms represented by 50% thermal ellipsoids. The lattice thf molecules and hydrogen atoms have been omitted for clarity. **1** Eu(1)-N(1) 2.571(5), Eu(1)-N(2) 2.491(6), Eu(1)-N(3) 2.509(5), Eu(1)-N(4) 2.459(6), Eu(1)-N(5) 2.431(6), Eu(1)-N(6) 2.577(5), Eu(1)-O(1) 2.590(5), Eu(1)-F(1) 2.302(4), Eu(1)-F(1)# 2.299(4), C(13)-Eu(1)-C(28) 93.93, N(1)-Eu(1)-N(6) 158.80(19), O(1)-Eu(1)-N(1) 73.02(18), O(1)-Eu(1)-N(6) 92.63(19), Eu(1)-F(1)-Eu(1)# 141.23(18); **2** Eu(2)-N(7) 2.550(5), Eu(2)-N(8) 2.522(5), Eu(2)-N(9) 2.507(5), Eu(2)-N(10) 2.456(5), Eu(2)-N(11) 2.446(5), Eu(2)-O(2) 2.561(5), Eu(2)-O(3) 2.525(4), Eu(2)-F(2) 2.302(4), Eu(2)-F(2)# 2.309(4), C(57)-Eu(1)-C(72) 94.79, O(2)-Eu(2)-O(3) 87.43(17), O(2)-Eu(2)-N(7) 75.87(17), O(3)-Eu(2)-N(7) 157.04(17), Eu(2)-F(2)-Eu(2)# 141.46(17), symmetry code: 1-X,2-Y,1-Z; 1-X,1-Y,2-Z.

The X-ray structure of $[\text{Eu}_2(\text{tftpz})_4(\text{py})_2(\text{dme})_2(\mu\text{-F})_2]\cdot 2\text{dme}$ (**7**) showed a fluoride-bridged dimer (**Figure 3**) in which the nine-coordinate europium atom is coordinated by two tftpz ligands, *cisoid* py and dme molecules ($\text{Cen}(\text{dme})\text{-Eu}(1)\text{-N}(5)$ 120.70°) and two bridging fluoride ligands. The average Eu-F bond length of the dinuclear complex **7** is 2.269(7) Å are longer than those of nine-coordinate $[\text{Yb}(\text{Cp})_2\text{F}(\text{thf})_2]$ (2.188 Å) and $[\text{Yb}(\text{MeCp})_2\text{F}(\text{thf})_2]$ (2.201 Å).^[29] The difference is consistent with the difference in lanthanoid ionic radii.^[30]

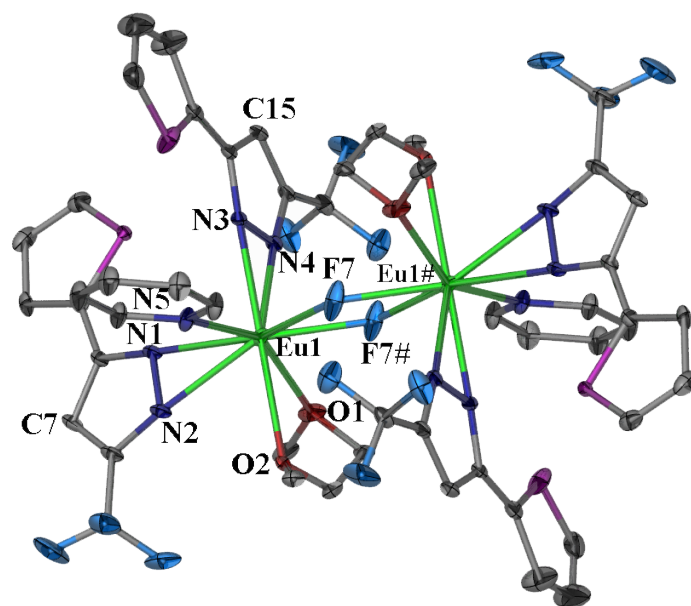


Figure 3. Molecular diagram of $[\text{Eu}_2(\text{tfpz})_4(\text{py})_2(\text{dme})_2(\mu\text{-F})_2] \cdot \text{dme}$ (**7**) with non-hydrogen atoms represented by 30% thermal ellipsoids. The lattice dme molecules and hydrogen atoms have been omitted for clarity. Eu(1)-N(1) 2.499(5), Eu(1)-N(2) 2.522(5), Eu(1)-N(3) 2.434(4), Eu(1)-N(4) 2.443(4), Eu(1)-N(5) 2.565(4), Eu(1)-O(1) 2.462(4), Eu(1)-O(2) 2.615(10), Eu(1)-F(7) 2.288(5), Eu(1)-F(7)# 2.250(5), C(7)-Eu(1)-C(15) 98.44, Cen(dme)-Eu(1)-N(5) 120.70, Eu(1)-F(7)-Eu(1)# 140.92(17), symmetry code: 1-X,1-Y,1-Z.

$[\text{Eu}_2(t\text{Bu}_2\text{pz})_4(\text{dme})_2(\mu\text{-F})_2]$ (**8**) crystallized in the triclinic space group $P\bar{1}$. Both Eu atoms are bridged by two fluoride atoms, forming a $[\text{Eu}_2\text{F}_2]$ core. A similar core has been seen previously in eight-coordinate $[\text{Ln}(\text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3})_2\text{F}]_2$ (Ln = La, Nd, Sm, Gd)^[31] and $[\text{Nd}(p\text{-HC}_6\text{F}_4\text{N}(\text{CH}_2)_2\text{NEt}_2)_2\text{F}]_2$.^[32] Each seven-coordinate europium ion is coordinated by two η^2 -fashion $t\text{Bu}_2\text{pz}$ ligands, one dme molecule and two bridging two bridging fluoride ligands. (**Figure 4**). The average Eu-F bond lengths 2.305(6) Å are near those of $[\text{Nd}(\text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3})_2\text{F}]_2$ (2.336 Å)^[31] and $[\text{Nd}(p\text{-HC}_6\text{F}_4\text{N}(\text{CH}_2)_2\text{NEt}_2)_2\text{F}]_2$ (2.305 Å).^[32]

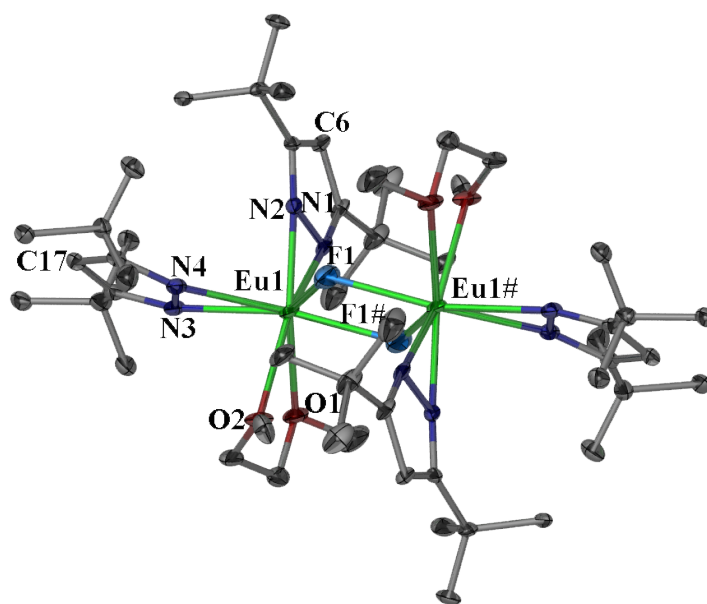


Figure 4. Molecular diagram of $[\text{Eu}_2(\text{tBu}_2\text{pz})_4(\text{dme})_2(\mu\text{-F})_2]$ (**8**) with non-hydrogen atoms represented by 30% thermal ellipsoids. The lattice hydrogen atoms have been omitted for clarity. Eu(1)-N(1) 2.404(4), Eu(1)-N(2) 2.444(4), Eu(1)-N(3) 2.397(4), Eu(1)-N(4) 2.422(4), Eu(1)-O(1) 2.577(4), Eu(1)-O(2) 2.564(5), Eu(1)-F(1) 2.279(4), Eu(1)-F(1) # 2.330(4), C(6)-Eu(1)-C(17) 87.92(11), Eu(1)-F(1)-Eu(1)# 109.40(16), symmetry code: 1-X,1-Y,1-Z.

$[\text{Eu}_6(\text{Me}_2\text{pz})_{10}(\text{thf})_6(\mu\text{-F})_2]$ (**9**) crystallized in the monoclinic space group $C2/c$ as a centrosymmetric hexanuclear cage (**Figure 5a**) with an ovoid core of Eu atoms and donor atoms (**Figure 5b**) linked by bridging fluoride (F1,1*), thf (O3), and pyrazolate ligands, with additional terminal pyrazolate (N5,6 and N9,10) and thf (O1, O2) donors. Pyrazolate moieties N1,2 and N7,8 are bound in a $\mu_3\text{-}1\eta^2(\text{N}_2);2\kappa(\text{N}):3\kappa(\text{N}')$ manner and ligand N3,4 in a rare $\mu_4\text{-}1\eta^5(\text{N}_2\text{C}_3) 2\eta^2(\text{N}_2):3\kappa(\text{N}):4\kappa(\text{N}')$ mode (**Figure 5c**), which has only been previously observed in $[\text{Ce}_4(\text{Me}_2\text{pz})_{12}]^{[33]}$ and in $[\text{K}_2\{\text{Mn}_2(\text{CO})_6\}_2(\text{pz})_6(\text{Et}_2\text{O})_2]^{[34]}$. Proposed η^5 coordination of ligand N_2C_3 (N3,4 and C7-9) to Eu, is supported by Eu3*-C7-9 distances of 3.006(6) – 3.058(6) Å, which are similar to those of $\pi\text{-}\eta^6\text{-Ph-La}$ bonds (2.979(10)-3.164(9)Å in six coordinate $[\text{La}(\text{OAr})_2(\mu\text{-OAr})_2]^{[35]}$ with allowance for different Ln^{3+} ionic radii and coordination numbers,^[30] and are near those of $\eta^5\text{-pz}$ coordination in $[\text{Eu}_4(\text{tBu}_2\text{pz})_8]^{[36]}$ after allowing for the effect of different oxidation states^[30] The values are far shorter than the sum of the van der Waals radius of an aromatic ring^[37] plus the metallic radius (pseudo van der Waals radius) of Eu (3.8 Å).^[38] In addition, the N3,4C7-9 ring is near normal to the Eu-ring centroid vector (Eu-centroid-ring N or C angles 86.84 – 92.53°), consistent with η^5 bonding.

Eu1 is nine coordinate and is bound by two bridging η^2 Me_2pz ligands (N1N2, N7N8), two bridging $\kappa(\text{N})$ Me_2pz ligands (N3,4*), two bridging fluoride ligands (F1, F1*) and one terminal

thf molecule(O1) (**Figure S8a**). Eu2 is also nine coordinate, with one terminal Me₂pz ligand (N5,6), one bridging η^2 Me₂pz ligand (N3,4), two bridging nitrogens (N1*, N8), and one bridging fluoride ligand (F1), one bridging thf molecule (O3) and one terminal thf molecule (O2) (**Figure S8b**). The nine-coordinate Eu3 atom is chelated by one terminal Me₂pz ligand (N9,10), η^5 -ligated by the N3*N4*C7*C8*C9* ring-of the μ_4 - η^5 -2 η^2 :3 κ :4 κ ligand, and bound by two bridging nitrogens of two μ_3 - κ :2 κ :3 η^2 Me₂pz ligands (N2*, N7), one bridging fluoride ligands (F1) and one bridging thf molecule (O3) (**Figure S8c**). The Eu–N bond lengths decrease in the series η^5 -Me₂pz [average 2.953(5) Å] > η^2 (bridging)-Me₂pz [average 2.820(5) Å] > κ (bridging)-Me₂pz [average 2.752(5) Å] > η^2 (terminal)-Me₂pz [average 2.560(5) Å]. Bridging tetrahydrofuran has been previously observed in a few [Ln(Me₂pz)₃(thf)₂] (Ln = Nd, Ho, Lu, Y, Ce) complexes,^[39] but is generally uncommon.

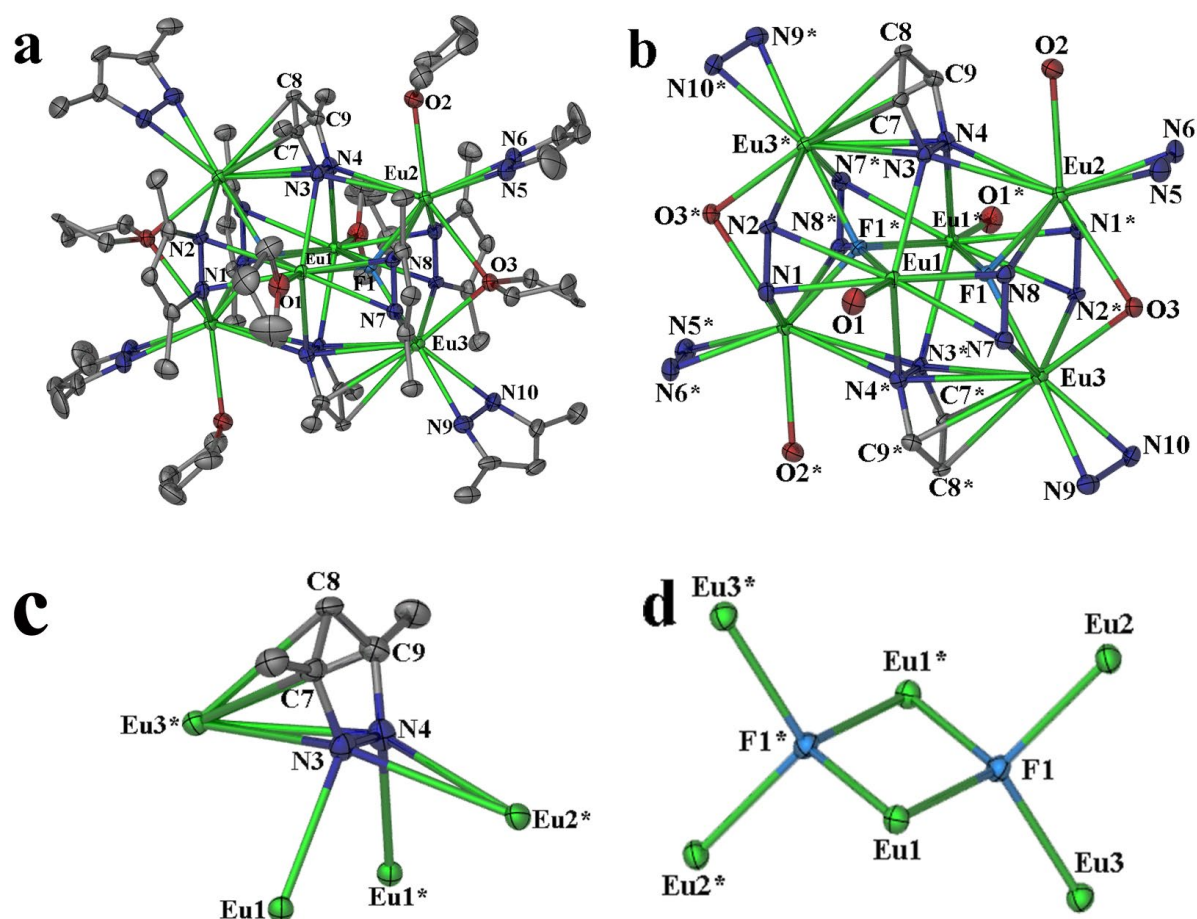
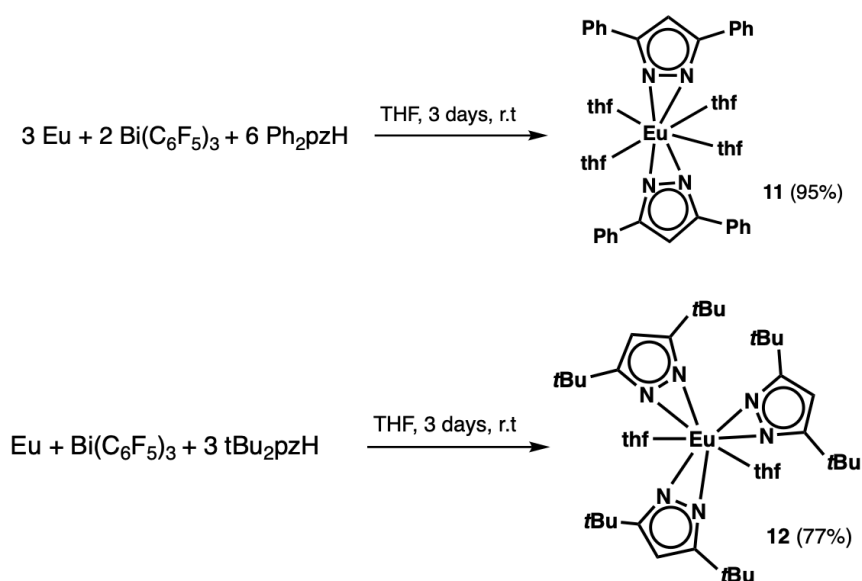


Figure 5. a. Molecular diagrams of [Eu₆(Me₂pz)₁₀(thf)₆(μ -F)₂] (**9**) with non-hydrogen atoms represented by 50% thermal ellipsoids. The lattice hydrogen atoms have been omitted for clarity; b. Framework of complex 9; c. The binding model of ligand N3,4; d. The cut-out of the Eu-F core. **Eu1** Eu(1)-N(1) 2.694(5), Eu(1)-N(2) 2.825(4), Eu(1)-N(3) 2.732(4), Eu(1)-N(4)* 2.764(5), Eu(1)-N(7) 2.832(5), Eu(1)-N(8) 2.698(5), Eu(1)-O(1) 2.617(4), Eu(1)-F(1) 2.415(3), Eu(1)-F(1)* 2.426(3); **Eu2** Eu(2)-N(1)* 2.757(5), Eu(2)-N(3) 2.937(4), Eu(2)-N(4) 2.931(5),

Eu(2)-N(5) 2.588(5), Eu(2)-N(6) 2.554(5), Eu(2)-N(8) 2.740(5), Eu(2)-O(2) 2.670(4), Eu(2)-O(3) 2.812(4), Eu(2)-F(1) 2.430(3); **Eu3** Eu(3)-N(2)* 2.732(5), Eu(3)-N(3)* 2.959(4), Eu(3)-N(4)* 2.946(5), Eu(3)-C(7)* 3.048(6), Eu(3)-C(8)* 3.058(6), Eu(3)-C(9)* 3.006(6), Eu(3)-N(7) 2.768(5), Eu(3)-N(9) 2.548(5), Eu(3)-N(10) 2.553(5), Eu(3)-O(3) 2.629(4), Eu(3)-F(1) 2.413(3). Eu(3)-centroid-C(7)* 92.53, Eu(3)-centroid-C(8)* 92.39, Eu(3)-centroid-C(9)* 90.35, Eu(3)-centroid-N(3)* 87.86, Eu(3)-centroid-N(4)* 86.84, symmetry code: 3/2-X,1/2-Y,1-Z.

Synthesis of europium pyrazolates using $\text{Bi}(\text{C}_6\text{F}_5)_3$

The pyrazolatoeuropium(II) complex $[\text{Eu}(\text{Ph}_2\text{pz})_2(\text{thf})_4]$ (**11**) and the pyrazolatoeuropium(III) complex $[\text{Eu}(\text{tBu}_2\text{pz})_3(\text{thf})_2]$ (**12**) were prepared by RTP reactions between an excess of lanthanoid metal, $[\text{Bi}(\text{C}_6\text{F}_5)_3] \cdot 0.5\text{diox}$ (diox = 1, 4-dioxane) and Ph_2pzH and tBu_2pzH stirred in thf at room temperature (Scheme 7). The reaction mixtures were monitored by ^{19}F NMR spectroscopy showing consumption of $\text{Bi}(\text{C}_6\text{F}_5)_3$ and formation of $\text{C}_6\text{F}_5\text{H}$ on completion of reaction. The oxidation state outcomes corresponding to those for use of $[\text{Ag}(\text{C}_6\text{F}_5)(\text{py})]$ in pyridine. Good yields (95 and 77 %) of crystalline products were obtained after the filtrates were evaporated to half volume under vacuum. Both **11** and **12** crystallized as thf complexes with satisfactory microanalyses.



Scheme 7 RTP reactions of Eu, $\text{Bi}(\text{C}_6\text{F}_5)_3$ and pzH in thf

Molecular structures

$[\text{Eu}(\text{Ph}_2\text{pz})_2(\text{thf})_4]$ (**11**) crystallizes in the triclinic space group $P-1$ with eight coordinate Eu having two η^2 - Ph_2Pz ligands and four coordinated thf molecules (**Figure 6** left). The two pyrazolatoligands display a *transoid* orientation ($\text{C}(8)\text{-Eu-C}(23)$ $151\text{-}152^\circ$) with four thf

donors in equatorial positions. The stereochemistry can be described as distorted octahedral if the point of attachment of the metal to the pyrazolate ligand is taken as midway along the N-N vector. The O-Eu-O angles between adjacent thf donors range from $71.3(3)^\circ$ to $131.2(3)^\circ$. The Eu-O (thf) distances are between 2.577(8) and 2.657(9) Å, which is similar to the Eu-O (thf) bond length of divalent $\text{EuI}_2(\text{thf})_5$ (2.58(2)-2.65(2) Å)^[40] and the average Eu-O (thf) bond length of $[\text{Eu}_2(\text{NCS})_4(\text{thf})_8]$ (2.667 Å).^[41] $[\text{Eu}(t\text{Bu}_2\text{pz})_3(\text{thf})_2]$ (**12**) crystallizes in the monoclinic space group $P2_1/n$ with three η^2 - $t\text{Bu}_2\text{Pz}$ ligands and two *transoid* thf ligands (O-Ln-O *ca.* 149°) (Figure 6 right) and the three η^2 - $t\text{Bu}_2\text{pz}$ ligands have a distorted *mer* arrangement (see backbone C-Eu-C angles in Figure 6).

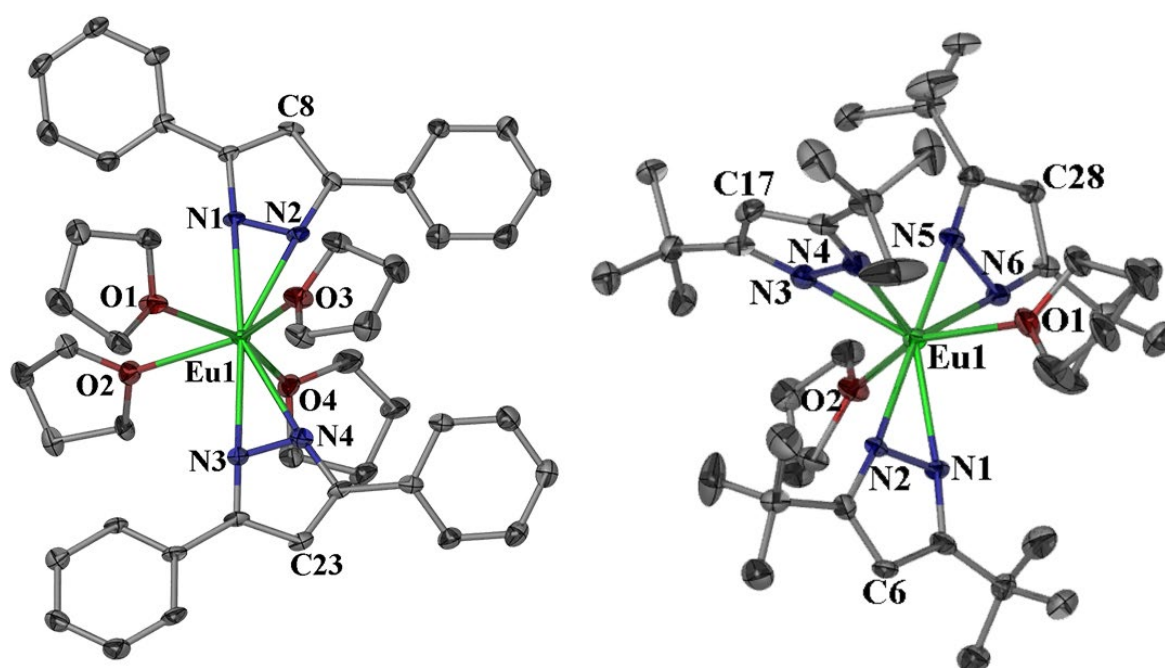


Figure 6. Molecular diagrams of $[\text{Eu}(\text{Ph}_2\text{pz})_2(\text{thf})_4]$ (**11**) (left) and $[\text{Eu}(t\text{Bu}_2\text{pz})_3(\text{thf})_2]$ (**12**) (right) with non-hydrogen atoms represented by 50% thermal ellipsoids. The hydrogen atoms have been omitted for clarity (Data for molecules 2 of **11** and **12** in supplementary information). **11** Eu1 Eu(1)-N(1) 2.597(8), Eu(1)-N(2) 2.551(8), Eu(1)-N(3) 2.550(8), Eu(1)-N(4) 2.562(8), Eu(1)-O(1) 2.640(7), Eu(1)-O(2) 2.580(7), Eu(1)-O(3) 2.663(7), Eu(1)-O(4) 2.580(7), C(8)-Eu(1)-C(23) 152.815; **12** Eu1 Eu(1)-N(1) 2.443(5), Eu(1)-N(2) 2.372(5), Eu(1)-N(3) 2.402(5), Eu(1)-N(4) 2.373(5), Eu(1)-N(5) 2.367(5), Eu(1)-N(6) 2.427(5), Eu(1)-O(1) 2.448(5), Eu(1)-O(2) 2.445(4), O(1)-Eu(1)-O(2) 149.04(17), C(6)-Eu(1)-C(17) 105.21, C(6)-Eu(1)-C(28) 145.30, C(17)-Eu(1)-C(28) 109.32.

Conclusions

Pentafluorophenylsilver in conjunction with europium metal and pyrazoles introduces new solvent-dependent outcomes into RTP syntheses of lanthanoid pyrazolates. In pyridine, a neglected solvent for such reactions, several lanthanoid(II) pyrazolates **1-3** and a

formamidinate **5** were obtained in high yields, but *t*Bu₂pzH gave the lanthanoid(III) complex [Eu(*t*Bu₂pz)₃(py)₂] **4**. Contrastingly, all corresponding syntheses of pyrazolates in thf led to C-F activation by a route involving C-F activation of pentafluorobenzene by Eu metal, generally giving [Eu^{III}₂(pz)₄(μ-F)₂(solv)_n] complexes **6-8**. C-F activation has not previously been observed in RTP reactions with AgC₆F₅. Surprisingly, Me₂pzH gave an hexanuclear Eu^{II} cage [Eu₆(Me₂pz)₁₀(μ-F)₂(thf)₆]. The structure features bridging fluoride, thf, and pyrazolate ligands, the last including the rare μ₄₋₁η⁵(N₂C₃) 2η²(N₂):3κ(N):4κ(N') binding mode, which links four Eu atoms, and is resistant to further oxidation. The RTP reaction of Eu, AgC₆F₅, and the very bulky DippFormH yields divalent [Eu(DippForm)₂(thf)₂] **10** without any C-F activation, despite a possible steric induced activation pathway being available. RTP reactions of Eu, Bi(C₆F₅)₃, and Ph₂pzH or *t*Bu₂pzH in thf do not involve C-F activation in contrast to AgC₆F₅, but lead to the same divergent oxidation state outcomes as observed with AgC₆F₅ in pyridine. This study opens a range of further synthetic opportunities. Pyridine appears to have considerable potential as an RTP (and RT) solvent and metal-induced pyridine coupling does not appear to be a problem under the mild conditions used in the present study, and the use should be extended to Bi(C₆F₅)₃. C-F activation involving Eu and AgC₆F₅ should be applicable to other ligand systems, but the lack of activation with DippFormH suggests steric limitations. The C-F activation with Eu, pyrazoles and AgC₆F₅ in thf contrasts the behaviour of other Ln metals, [8] but may extend to them with other ligand systems.

Experimental

General

The lanthanoid compounds described here are highly air and moisture sensitive, and were prepared and handled with vacuum-nitrogen line techniques and in a dry box under an atmosphere of purified nitrogen. Europium metal was from Eutectix. Large chunks were filed in the drybox before use. AgC₆F₅ [8] and Bi(C₆F₅)₃ [4] were synthesized by the reported methods. All other chemicals were purchased from Sigma Aldrich. Solvents (thf and dme) were pre-dried by distillation over sodium or sodium benzophenone ketyl before being stored under an atmosphere of nitrogen. Pyridine was distilled over potassium hydroxide, degassed and stored over dried 4Å molecular sieves. Other chemicals were used without further purification. IR spectra were recorded as Nujol mulls between NaCl plates using an ATIR instrument within the range 4000–700 cm⁻¹. Proton decoupled ¹⁹F NMR spectra were recorded with a Bruker DPX 300MHz spectrometer or a Bruker 400MHz instrument. Chemical shifts were referenced

to the residual ^1H resonances of the deuterated solvents (^1H). The Raman spectrum of **9** was obtained for a sample scaled in a capillary with a Renishaw Invia Raman microscope at an excitation line of 504nm using an Argon ion laser. Microanalyses were determined by the Elemental Analysis Service, London Metropolitan University, and all the samples were sealed in tubes under nitrogen. Crystals were immersed in crystallography oil, and were measured on a Bruker X8 APEXII SCXRD or the MX1 beamlines at the Australian Synchrotron. Crystal data and refinement details are given in **Table S1**. CCDC number 2117838-2117847 for compound 1-4, 6-9 and 11-12, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Europium complexes by using AgC_6F_5 in py

General procedure Europium metal powder (2.00 mmol), pentafluorophenyl(pyridine)silver (I) ($\text{AgC}_6\text{F}_5(\text{py})$) (0.50 mmol) and ligands (Ph_2pzH , ttfpzH , PhMepzH , $t\text{Bu}_2\text{pzH}$ and DFFormH) (0.50 mmol) were stirred in dry py (10 ml) under nitrogen for 2 days at room temperature. Occurrence of reaction was often indicated by formation of a silver mirror. Silver mirrors on the reaction flask were cleaned by dissolution in dilute HNO_3 and some cases tested for silver by addition of HCl . The filtrates were evaporated to half volume under vacuum and the crystals were obtained.

$[\text{Eu}(\text{ph}_2\text{pz})_2(\text{py})_4]\cdot 2\text{py}$ 1

Red crystals (0.219, 82%), Found C, 66.18; H, 4.47; N, 11.83; $\text{C}_{50}\text{H}_{42}\text{EuN}_8$ (loss two py, 906.88) requires C, 66.22; H, 4.67; N, 12.36 %. IR (Nujol): 1597m, 1574w, 1261vs, 1217m, 1095vs, 1022vs, 971m, 910w, 865m, 800vs, 757m, 701s cm^{-1} .

$[\text{Eu}(\text{ttfpz})_2(\text{py})_4]$ 2

Red crystals (0.203, 90%), Found C, 47.88; H, 3.05; N, 12.52; $\text{C}_{36}\text{H}_{28}\text{EuF}_6\text{N}_8\text{S}_2$ (902.74) requires C, 47.90; H, 3.13; N, 12.41 %. IR (Nujol): 1620w, 1572w, 1598s, 1508m, 1306m, 1239vs, 1217m, 1162s, 1109vs, 1074s, 1034s, 979s, 923m, 881m, 844s, 790vs, 752s 702vs cm^{-1} .

$[\text{Eu}(\text{PhMepz})_2(\text{py})_4]$ 3

Red crystals (0.120, 61%), Found C, 61.16; H, 4.77; N, 14.53; $\text{C}_{40}\text{H}_{38}\text{EuN}_8$ (782.74) requires C, 61.38; H, 4.89; N, 14.32 %. IR (Nujol): 1592s, 1270m, 1215s, 1150m, 1069s, 1018s, 1000s, 962s, 914m, 883m, 754vs, 701vs cm^{-1} .

[Eu(*t*Bu₂pz)₃(py)₂] 4

Colourless crystals (0.107, 76%), Found C, 59.43; H, 7.77; N, 12.89; C₄₃H₆₇EuN₈ (848.00) requires C, 60.90; H, 7.96; N, 13.21 %. IR (Nujol): 1597w, 1572w, 1500m, 1313w, 1286m, 1251s, 1223m, 1205w, 1129m, 1068m, 1036m, 1002s, 937m, 850w, 806s, 752m, 724m, 702s cm⁻¹.

[Eu(DFForm)₂(py)₃] 5

Orange crystals (0.198, 86%), Found C, 53.14; H, 3.28; N, 10.43; C₄₁H₂₉EuF₈N₇ (923.67) requires C, 53.31; H, 3.16; N, 10.61 %. IR (Nujol): 1663m, 1618w, 1594w, 1569m, 1312m, 1262m, 1205m, 1149m, 1096m, 1063m, 1033w, 1008m, 992m, 880w, 822m, 803m, 774s, 741m, 721m, 702s cm⁻¹. **5** crystallized in the monoclinic space group C2/c, a = 12.894(3) Å, b = 17.326(4) Å, c = 18.041(4) Å, β = 107.64(3)°, V = 3841.2(15) Å³, which had unit cell parameters in agreement with the reported structure,^[25] monoclinic space group C2/c, a = 12.8569(3) Å, b = 17.2704(4) Å, c = 18.0267(5) Å, β = 107.775(1)°, V = 3811.64(17) Å³.

Synthesis of Europium complexes by using AgC₆F₅ in thf

General procedure Europium metal powder (2.00 mmol), pentafluorophenyl(pyridine)silver (I) (AgC₆F₅(py)) (0.50 mmol) and ligands (Ph₂pzH, ttfpzH, *t*Bu₂pzH, Me₂pzH and DippFormH) (0.50 mmol) were stirred in dry thf (10 ml) under nitrogen for 3 days at room temperature. After filtration of the reaction mixture, a small (0.3ml) aliquot was monitored by ¹⁹F NMR, and in the case of successful reactions. Occurrence of reaction was often indicated by formation of a silver mirror. Silver mirrors on the reaction flask were cleaned by dissolution in dilute HNO₃ and some cases tested for silver by addition of HCl. The filtrates were evaporated to half volume under vacuum. If crystallization did not occur on prolonged cooling, the crystallization method is described with the individual compounds.

[{Eu₂(Ph₂pz)₄(py)₄(thf)₂F₂}{Eu₂(Ph₂pz)₄(py)₂(thf)₄F₂}]·6thf 6

¹⁹F NMR (THF, ext. CFCl₃, ppm): δ = -134.7 ppm (m, 2F, F-2, 6), -135.3 ppm (m, 0.6F, -F), -150.9 ppm (m, 1F, F-4), -158.7 ppm (m, 2F, F-3, 5). Yellow crystals (0.193, 82%), (Found Eu, 16.12; C₁₉₈H₂₁₂Eu₄F₄N₂₂O₁₂ (3775.72) requires Eu, 16.09 %) were obtained after two weeks at -20 °C. IR (Nujol): 1634s, 1599vs, 1574w, 1506w, 1321w, 1261s, 1219s, 1175m, 1152m, 1069s, 1034s, 970s, 912m, 875m, 800s, 757vs cm⁻¹.

[Eu₂(ttfpz)₄(py)₂(dme)₂F₂]·2dme 7

¹⁹F NMR (THF, ext. CFCl₃, ppm) showed no presence of any F peaks. Yellow crystals (0.125,

64%), (Found Eu 18.40; C₅₄H₅₆Eu₂F₁₄N₁₀O₆S₄ (1639.24, lost one dme) requires Eu, 18.54 %) were obtained after the filtrate (which did not deposit crystals) was evaporated and the residua was recrystallized from dme. IR (Nujol): 1599w, 1511m, 1261vs, 1217m, 1162m, 1097vs, 1021vs, 979m, 926m, 863m, 801vs, 701vs cm⁻¹.

[Eu₂(*t*Bu₂pz)₄(dme)₂F₂] 8

¹⁹F NMR (THF, ext. CFCl₃, ppm): δ= -134.6 ppm (m, 2F, F-2, 6), -135.2 ppm (m, 0.6F, -F), -150.8 ppm (m, 1F, F-4), -158.6 ppm (m, 2F, F-3, 5). Colourless crystals (0.130 g, 84%), (Found Eu, 24.51; C₅₂H₉₆Eu₂F₂N₈O₄ (1239.28) requires Eu, 24.52 %) were obtained after the filtrate (which did not deposit crystals) was evaporated and the residua was recrystallized from dme. IR (Nujol): 1597m, 1570w, 1500m, 1316m, 1285m, 1250s, 1228m, 1205m, 1109s, 1063m, 1023s, 1002s, 934m, 858m, 806s, 754m, 725m, 701s cm⁻¹.

[Eu₆(Me₂pz)₁₀(thf)₆F₂] 9

¹⁹F NMR (THF, ext. CFCl₃, ppm): δ= -133.2 ppm (m, 2F, F-2, 6), 133.7 ppm (m, 1F), -149.3 ppm (m, 1F, F-4), -157.1 ppm (m, 2F, F-3, 5). Yellow-green crystals (0.085, 73%), (Found C, 38.16; H, 4.77; N, 11.53; C₇₄H₁₁₈Eu₆F₂N₂₀O₆ (2333.64) requires C, 38.09; H, 5.10; N, 12.00 %) were obtained after isolated half thf. IR (Nujol): 1576w, 1516m, 1304w, 1261vs, 1094vs, 1022vs, 865m, 801vs, 723w cm⁻¹. Raman: 3110m, 2963m, 2913s, 1562s, 1433s, 1024s, 592s, 490m, 422m, 348m, 141s cm⁻¹.

[Eu(DippForm)₂(thf)₂]·2thf 10

¹⁹F NMR (THF, ext. CFCl₃, ppm): δ= -138.9 ppm (m, 2F, F-2, 6), -155.0 ppm (m, 1F, F-4), -162.9 ppm (m, 2F, F-3, 5), which confirmed pentafluorobenzene formed during the reaction. Yellow crystals (0.206, 71%) (Found: C, 66.54; H, 8.42; N, 4.82; C₆₆H₁₀₂EuN₄O₄ (1167.50) requires C, 67.90; H, 8.81; N, 4.80 %) were obtained after isolated half thf. **10** crystallized in the triclinic space group *P*-1, *a*=14.2270(15) Å, *b*=14.2371(16) Å, *c*=18.620(2) Å, α=70.702(4)°, β=69.341(4)°, γ=66.186(4)°, *V*=3149.7(6) Å³, which is similar to that reported, ^[15] triclinic space group, reduced cell: *a*=14.292 Å, *b*=14.292 Å, *c*=19.000 Å, α=69.75°, β=69.75°, γ=66.04°. IR (Nujol): 1656w, 1595m, 1316s, 1255m, 1183s, 1099s, 1074s, 1037s, 1014w, 932m, 879m, 801s, 803vs, 753s, 722m, 703m cm⁻¹.

Synthesis of europium pyrazolates by using Bi (C₆F₅)₃

General procedure Europium metal powder (1.00 mmol), trispentafluorophenylbismuth Bi(C₆F₅)₃ (0.25 mmol) and pyrazole (Ph₂pzH and *t*Bu₂pzH) (0.75 mmol) were stirred in dry thf

(10 ml) under nitrogen for 3 days at room temperature. After filtration of the reaction mixture, a small (0.3ml) aliquot was monitored by ^{19}F NMR, and in the case of successful reactions, **11** and **12** showed characteristic resonances of pentafluorophenylbenzene, ^{19}F NMR (THF, ext. CFCl_3 , ppm): $\delta = -138.0$ (m, 2F, F-2, 6), -154.2 (m, 1F, F-4), -162.0 (m, 2F, F-3, 5). The filtrates were evaporated to half volume under vacuum.

[Eu(Ph₂pz)₂(thf)₄] 11

Yellow crystals (0.209g, 95%), M.p. 226-228 °C, (Found C, 62.63; H, 5.97; N, 6.54; $\text{C}_{46}\text{H}_{54}\text{EuN}_4\text{O}_4$ (878.89) requires C, 62.86; H, 6.19; N, 6.37 %) were obtained at -20 °C after three days. IR (Nujol): 1602s, 1527w, 1513m, 1293w, 1261vs, 1218m, 1173w, 1042vs, 968s, 903s, 872m, 800s, 754vs, 722w, 702s cm^{-1} .

[Eu(*t*Bu₂pz)₃(thf)₂] 12

Colourless crystals (0.165g, 77%), M.p. 140-142 °C, (Found C, 58.95; H, 8.78; N, 10.00; $\text{C}_{41}\text{H}_{73}\text{EuN}_6\text{O}_2$ (834.01) requires C, 59.04; H, 8.82; N, 10.08 %) were obtained at -20 °C after one week. IR (Nujol): 1566m, 1503s, 1312m, 1258s, 1205m, 1095s, 1023s, 917m, 874m, 802s, 725m cm^{-1} .

Acknowledgements

GBD and PCJ gratefully acknowledge the ARC for funding (DP190100798). This research was undertaken in part using the MX1 beamline at the Australian Synchrotron, part of ANSTO.^[42]

References:

- [1]. G. B. Deacon, C. M. Forsyth, S. Nickel, *J. Organomet. Chem.*, **2002**, *647*, 50–60
- [2]. G. B. Deacon, M. E. Hossain, P. C. Junk, M. Salehisaki. *Coord. Chem. Rev.*, **2017**, *340*, 247-265.
- [3]. (a) Z. Guo, R. Huo, Y. Q. Tan, V. Blair, G. B. Deacon, P. C. Junk, *Coord. Chem. Rev.*, **2020**, *415*, 213232, 1-23; (b) J. Hitzbleck, G.B. Deacon, K. Ruhlandt-Senge, *Eur. J. Inorg. Chem.*, **2007**, 592-601; (c) G. B. Deacon, C. M. Forsyth, B. M. Gatehouse, P. A. White, *Aust. J. Chem.* **1990**, *43*, 795-806; (d) S. Hauber, M. Niemeyer, *Inorg. Chem.*, **2005**, *44*, 8644-8646; (e) G. B. Deacon, P. C. Junk, G. J. Moxey, *Chem. Asian. J.*, **2009**, *4*, 1717-1728; (f) G. B. Deacon, E. E. Delbridge, B. W. Skelton, A. H. White, *Eur. J. Inorg. Chem.* **1999**, 751-761.
- [4]. Z. Guo, V. Blair, G. B. Deacon, P. C. Junk, *Chem. Eur. J.* **2018**, *24*, 17464-17474.
- [5]. Z. Guo, V. Blair, G. B. Deacon, P. C. Junk, *Dalton Trans.* **2020**, *49*, 13588–13600.
- [6]. M. M. Gillett-Kunnath, J. G. MacLellan, C. M. Forsyth, P. C. Andrews, G. B. Deacon, K. Ruhlandt-Senge, *Chem. Commun.* **2008**, 4490-4492.
- [7]. Y. Takahashi, A. O'Brien, G. B. Deacon, P. C. Andrews, M. Wolf, A. Torvisco, M. M. Gillett-Kunnath, K. Ruhlandt-Senge, *Inorg. Chem.* **2017**, *56*, 11480-11489.
- [8]. Z. Guo, J. Luu, V. Blair, G. B. Deacon, P. C. Junk, *Eur. J. Inorg. Chem.* **2019**, 1018-1029.
- [9]. (a) T. Simler, T. J. Feuerstein, R. Yadav, M. T. Gamer, P. W. Roesky, *Chem. Commun.* **2019**, *55*, 222-225; (b) N. Schwarz, X. Sun, R. Yadav, R. Koppe, T. Simler, P. W. Roesky, *Chem. Eur. J.* **2021**, *27*, 12857-12865; (c) L. M. Aguirre Quintana, N. Jiang, J. Bacsá, H. S. La Pierre, *Dalton Trans.*, **2020**, *49*, 5420–5423.
- [10]. EuII (a) J. Garcia, M. J. Allen, *Eur. J. Inorg. Chem.* **2012**, 4550–4563; EuIII (b) G. Vicentini, L. B. Zinner, J. Zukerman-Schpector, K. Zinner, *Coord. Chem. Rev.*, **2000**, *196*, 353-382; (c) Y. Ma, Y. Wang, *Coord. Chem. Rev.*, **2010**, *254*, 972-990.
- [11]. (a) J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373-431; (b) H. Plenio, *Chem. Rev.* **1997**, *97*, 3363–3384; (c) H. Plenio, *ChemBioChem*, **2004**, *5*, 650–655; (d) H. Yin, A. V. Zabula, E. J. Schelter, *Dalton Trans.*, **2016**, *45*, 6313-6323; (e) O. Eisenstein, J. Milani, R. N. Perutz, *Chem. Rev.*, **2017**, *117* (13), 8710-8753; (f) J. H. Farnaby, T. Chowdhury, S. J. Horsewill, B. Wilson, F. Jaroschik, *Coord. Chem. Rev.*, **2021**, *437*, 213830, 1-84.
- [12]. (a) J. P. Vizuet, M. L. Mortensen, A. L. Lewis, M. A. Wunch, H. R. Firouzi, G. T. McCandless, K. J. Balkus Jr. *J. Am. Chem. Soc.* **2021**, <https://doi.org/10.1021/jacs.1c10493>; and references therein. (b) G. B. Deacon, A. J. Koplick, W. D. Raverty, D. G. Vince, *J. Organomet. Chem.* **1979**, *182*, 121-141; (c) G. B. Deacon, P. I. MacKinnon, T. D. Tuong, *Aust. J. Chem.* **1983**, *36*, 43-53; (d) L. Maron, E. L. Werkema, L. Perrin, O. Eisenstein, R. A. Andersen, *J. Am. Chem. Soc.* **2005**, *127*, 279-292; (e) E. L. Werkema, R. A. Andersen, *J. Am. Chem. Soc.* **2008**, *130*, 7153-7165; (f) G. B. Deacon, C. M. Forsyth, P. C. Junk, J. Wang, *Chem. Eur. J.* **2009**, *15*, 3082-3092; (g) G. B. Deacon, P. C. Junk, R. P. Kelly, J. Wang, *Dalton Trans.*, **2016**, *45*, 1422-1435; (h) P. L. Watson, T. H. Tulip, I. Williams, *Organometallics.* **1990**, *9*, 1999-2009; (i) B. K. Ling, Y. Q. Zhai, H. K. Hsu, Y. T. Chan, W. P. Chen, t. han, Y. Z. Zheng, *Chem. Commun.*, **2020**, *56*(64), 9130-9133; (j) W. Huang, P. L. Diaconescu, *Organometallics*, **2017**, *36*, 89–96; (k) T. Kumar, F. Massicot, D. Harakat, S. Chevreux, A. Martinez, K. Bordolinska, P. Preethalayam, R. K. Vasu, J. Behr, J. Vasse, F. Jaroschik, *Chem. Eur. J.*, **2017**, *23*, 16460-16465; (l) T. Kumar, Y. Yang, S. Sghaier,

- Y. Zaid, X. F. Le Goff, E. Rousset, F. Massicot, D. Harakat, A. Martinez, M. Taillefer, L. Maron, J. Behr, F. Jaroschik, *Chem. Eur. J.*, **2021**, *27*, 4016-4021; (m) G. B. Deacon, G. D. Fallon, C. M. Forsyth, S. C. Harris, P. C. Junk, B. W. Skelton, A. H. White, *Dalton Trans.*, **2006**, 802-812.
- [13]. (a) G. M. Badger, W. H. F. Sasse, *Advances in Heterocyclic Chemistry*, **1963**, *2*, 179-202; (b) S. Yamada, T. Kaneda, P. Steib, K. Murakami, K. Itami, *Angew. Chem. Int. Ed.*, **2019**, *58*, 8341-8345 (c) T. Kawashima, T. Takao, H. Suzuki, *J. Am. Chem. Soc.*, **2007**, *129*, 11006-11007; (d) M. T. Robo, M. R. Prinsell, D. J. Weix, *J. Org. Chem.*, **2014**, *79*, 10624-10628; (e) E. C. Constable, C. E. Housecroft, *Molecules*, **2019**, *24*, 3951(1-38).
- [14]. (a) D. Pfeiffer, B. J. Ximba, L. M. Liable-Sands, A. L. Rheingold, M. J. Heeg, D. M. Coleman, H. B. Schlegel, T. F. Kuech, C. H. Winter, *Inorg. Chem.* **1999**, *38*, 4539-4548; (b) S. Beaini, G. B. Deacon, E. Delbridge, P. C. Junk, B. W. Skelton, A. H. White, *Eur. J. Inorg. Chem.* **2008**, 4586-4596.
- [15]. M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. Konstas, J. Wang, H. Bittig, D. Werner, *Chem. Eur. J.* **2013**, *19*, 1410-1420.
- [16]. G. B. Deacon, P. C. Junk, D. Werner, *Chem. Eur. J.* **2016**, *22*, 160-173.
- [17]. S. Beaini, G. B. Deacon, M. Hilder, P. C. Junk, D. R. Turner, *Eur. J. Inorg. Chem.* **2006**, 3434-3441.
- [18]. G. B. Deacon, P. C. Junk, A. Urbatsch, *Eur. J. Inorg. Chem.* **2011**, 3592-3600.
- [19]. G. B. Deacon, C. M. Forsyth, R. H. Newnham, T. D. Tuong, *Aust. J. Chem.* **1987**, *40*, 895-906.
- [20]. C. M. Forsyth, G. B. Deacon, *Organometallics* **2000**, *19*, 1205-1207.
- [21]. G. B. Deacon, T. Feng, P. MacKinnon, R. H. Newnham, S. Nickel, B. W. Skelton and A.H. White, *Aust. J. Chem.*, 1993, *46*, 387-399.
- [22]. G. B. Deacon, R. H. Newnham, *Aust. J. Chem.* **1985**, *38*, 1757-1765.
- [23]. G. B. Deacon, D. L. Wilkinson, *Inorg. Chim. Acta.* **1988**, *142*, 155-159.
- [24]. M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. Konstas, J. Wang, *Chem. Eur. J.* **2007**, *13*, 8092-8110.
- [25]. Z. Guo, V. Blair, G. B. Deacon, P. C. Junk, *Chem. Commun.* **2021**, *57*, 11513-11516.
- [26]. G. B. Deacon, F. Jaroschik, P. C. Junk, R. P. Kelly, *Chem. Commun.* **2014**, *50*, 10655-10657.
- [27]. R. P. Kelly. Advances in the organometallic and organoamidometallic chemistry of the lanthanoids and alkaline earths. Monash University, School of Chemistry, **2013**, PhD thesis.
- [28]. V. E. Mikhailov, Y. N. Chuklanova, E. B. Mikhailov, A. V. Sergeev, R. N. Shchelokov. *Russ. J. Inorg. Chem.*, **1998**, *43*, 1862-1864.
- [29]. (a) G. B. Deacon, S. C. Harris, G. Meyer, D. Stellfeldt, D. L. Wilkinson, G. Zelesny, *J. Organomet. Chem.* **1998**, *552*, 165-170; (b) G. B. Deacon, G. Meyer and D. Stellfeldt, *Eur. J. Inorg. Chem.* **2000**, 1061-1071.
- [30]. R. D. Shannon. *Acta. Cryst. B.* **1976**, *A32*, 751-767.
- [31]. Z. Xie, K. Chui, Q. Yang, T. C. W. Mak, J. Sun, *Organometallics*, **1998**, *17*, 3937-3944.
- [32]. G. B. Deacon, C. M. Forsyth, P. C. Junk, R. Kelly, A. Urbatsch, J. Wang, *Dalton Trans.* **2012**, *41*, 8624-8634.
- [33]. D. Werner, U. Bayer, N. E. Rad, P. C. Junk, G. B. Deacon, R. Anwender, *Dalton Trans.* **2018**, *47*, 5952-5955.

- [34]. T. Morawitz, F. Zhang, M. Bolte, J. W. Bats, H. Lerner, M. Wagner, *Organometallics*, **2008**, *27*, 5067-5074.
- [35]. R. J. Butcher, D. L. Clark, S. K. Grumbine, R. L. Vincent-Hollis, B. L. Scott, J. G. Watkin, *Inorg. Chem.* **1995**, *34*, 5468-5476.
- [36]. G. B. Deacon, A. Gitlits, P. W. Roesky, M. K. Bürgstein, K. C. Lim, B. W. Skelton, A.H. White, *Chem. Eur. J.* **2001**, *7*, 127-138.
- [37]. A. Bondi. *J. Phys. Chem.* **1964**, *68*, 441-451.
- [38]. A. F. Wells. *Structural Inorganic Chemistry*, Clarendon, Oxford, 5th ed., **1984**, p. 1288.
- [39]. (a) G. B. Deacon, B. M. Gatehouse, S. Nickel, S. N. Platts, *Aust. J. Chem.* **1991**, *44*, 613-621; (b) D. Werner, G. B. Deacon, P. C. Junk, R. Anwender, *Dalton Trans.* **2017**, *46*, 6265-6277; (c) G. B. Deacon, R. Harika, P. C. Junk, B. W. Skelton, D. Werner, A.H. White, *Eur. J. Inorg. Chem.* **2014**, 2412-2419.
- [40]. G. Heckmann, M. Niemeyer, *J. Am. Chem. Soc.*, **2000**, *122*, 4227-4228.
- [41]. J. M. Bakker, G. B. Deacon, C. M. Forsyth, P. C. Junk, M. Wiecko, *Eur. J. Inorg. Chem.* **2010**, 2813-2825.
- [42]. N. P. Cowieson, D. Aragao, M. Clift, D. J. Ericsson, C. Gee, S. J. Harrop, N. Mudie, S. Panjekar, J. R. Price, A. Riboldi-Tunnicliffe, R. Williamson, T. Caradoc-Davies, *J. Synchrotron Radiat.* **2015**, *22*, 187-190.