Dinuclear alkynyllanthanoid(II) dications with pentaphenylcyclopentadienyl or tri-*tert*-butyldiphosphacyclopentadienyl counter ions†

Craig M. Forsyth,[a] Glen B. Deacon,*[a] Leslie D. Field,[b] Cameron Jones,[c] Peter C. Junk,[a] Danielle L. Kay,[ab] Anthony F. Masters[b] and Anne F. Richards[ac]

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Reaction of [Yb(CpPh$_5$)(C≡CPh)(thf)]$_2$ (CpPh$_5$ = pentaphenylcyclopentadienyl), prepared from Yb(C≡CPh)$_2$ and HCpPh$_5$ or Yb metal, HgPh(C≡CPh) and HCpPh$_5$, with a controlled amount of diglyme (dig), and of Eu(C≡CPh)$_2$, P≡CBu^t and dig, yield the unusual organolanthanoid(II) dicationic complexes [Yb(C≡CPh)(dig)(thf)$_2$]$_2$[CpPh$_5$]$_2$·4thf and [Eu(C≡CPh)(dig)$_2$]$_2$[P$_2$C$_3$Bu^t$_3$]$_2$ respectively.

The emerging interest in the synthesis of organolanthanoid(III) cations,[1] fueled by the high reactivity of cationic group 4 metal d^0 complexes (*e.g* ML$_2$R$^+$),[2] has not been duplicated for analogous lanthanoid(II) species Ln^{II}R(S)$^+$.[3] These are mainly restricted to derivatives with a cyclopentadienyl ligand as the residual Ln–C moiety.[3a,b] The isolation of LnR(S)$^+$ species present particular difficulties due to the lack of a stabilizing anionic co-ligand and the propensity for ligand redistribution reactions leading to solvated Ln(S)$_n$$^{2+}$.[4] We now report the preparation of dinuclear alkynyllanthanoid(II) cations [Ln(CCPh)(S)]$_2$$^{2+}$ which are unique in having an alkynyl moiety as the σ-bound organic ligand. Our study also provides the first structurally characterised lanthanoid complexes of the very bulky CpPh$_5$ ligand.

Structural elucidation of the complex [Eu(μ–C≡CPh)(dig)$_2$]$_2$[P$_2$C$_3$Bu^t$_3$]$_2$·C$_6$H$_6$·(dig)$_{0.5}$ (**1**) (dig = diglyme), obtained as a few single crystals by addition of dig to the product mixture from the reaction of the phosphaalkyne P≡CBu^t with a thf solution of Eu(C≡CPh)$_2$ at −30 °C,‡ provided the first evidence of [Ln^{II}(C≡CR)(S)$_n$]$_2$$^{2+}$ species. The structure of **1**§ (Fig. 1) shows a dinuclear dication with two Eu(dig)$_2$ units bridged by two PhC≡C$^-$ ligands *via* the α-C atoms. The two diglyme ligands wrap around the naked face of the europium centres in a helical fashion. Each Eu is eight coordinate (bicapped trigonal prism), one higher than in the alkynyl bridged [EuCp*(μ-C≡CPh)(thf)$_2$]$_2$[5] which has marginally shorter Eu–C bonds, <Eu–C> (C≡CPh) 2.705(7) Å, and Eu–O bonds, <Eu–O> 2.62(1) Å. All the Eu–C distances in **1** are similar, but the Eu$_2$(μ-C≡CPh)$_2$ bonding is unsymmetrical, with one larger and one smaller Eu–C–C angle for each alkynyl (Fig. 1). The P$_2$C$_3$Bu^t$_3$ anions lie in the crystal lattice and do not interact with the metal centres, the first structurally characterised example of an unbound P$_2$C$_3$R$_3$$^-$ moiety. Despite wide-ranging reactivity with many organometallic species,[6] P≡CBu^t has been little studied with highly reactive organolanthanoids.[7] However, cyclisation of P≡CBu^t under metal vapour synthesis conditions has yielded the complexes [Ln(η^5-P$_2$C$_3$Bu^t$_3$)$_2$] (Ln = Sc, Yb),[7b,c] and metal induced oligomerisation of the phosphaalkyne giving a mixture of [P$_2$C$_3$Bu^t$_3$]$^-$ and [P$_3$C$_2$Bu^t$_2$]$^-$ is known.[8] Since the Eu^{II} oxidation state is maintained in forming **1**, and one alkynyl group/Eu is lost, the present oligomerisation may be accompanied by oxidative dimerisation to (PhC≡C)$_2$ (*cf.* oxidative dimerisation of P≡CBu^t),[7a] with only [P$_2$C$_3$Bu^t$_3$]$^-$ being isolated in **1**. Although no organometallic species was isolated from the reaction of P≡CBu^t with Yb(C≡CPh)$_2$, crystals of the known cage P$_5$C$_5$(Bu^t)$_5$ eventually deposited, evincing the initial presence of [P$_2$C$_3$Bu^t$_3$]$^-$ and [P$_3$C$_2$Bu^t$_2$]$^-$ in the product mixture.[9]

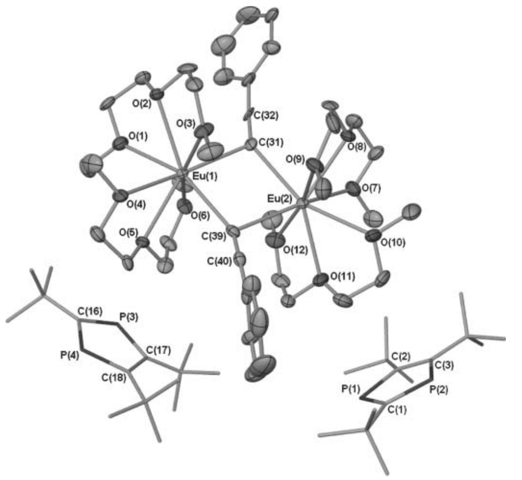

Fig. 1 Molecular structure of the dication of **1** shown with 50% thermal ellipsoids and a stick representation of the two P$_2$C$_3$Bu^t$_3$ anions. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Eu(1)–C(31) 2.72(1), Eu(1)–C(39) 2.74(1), Eu(2)–C(31) 2.77(1), Eu(2)–C(39) 2.73(1), Eu–O 2.664(6)–2.699(6), P–C 1.70(2)–1.79(1); Eu–C(31)–C(32) 147.0(8), 118.0(8), Eu–C(39)–C(40) 149.7(8), 113.9(8).

Given the complex, low-yielding nature of the phosphaalkyne system we investigated the use of the very bulky pentaphenylcyclopentadienyl (CpPh$_5$) for a deliberate synthesis of [Ln$_2$(μ-C≡CPh)$_2$(S)$_x$]$^{2+}$ dications (Scheme 1). The supracyclopentadienyl[10a] CpPh$_5$ ligand has been only sporadically used for

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[a] *School of Chemistry, Monash University, Clayton 3800, Australia. E-mail: glen.deacon@sci.monash.edu.au; Fax: +613 9905 4597; Tel: +613 9905 4568*
[b] *School of Chemistry, University of Sydney, Sydney 2006, Australia. Fax: +612 9531 3329; Tel: +612 9531 3743*
[c] *School of Chemistry, Cardiff University, Cardiff, UK CF10 3AT. Fax: +4429 20874030; Tel: +4429 2087 4060*

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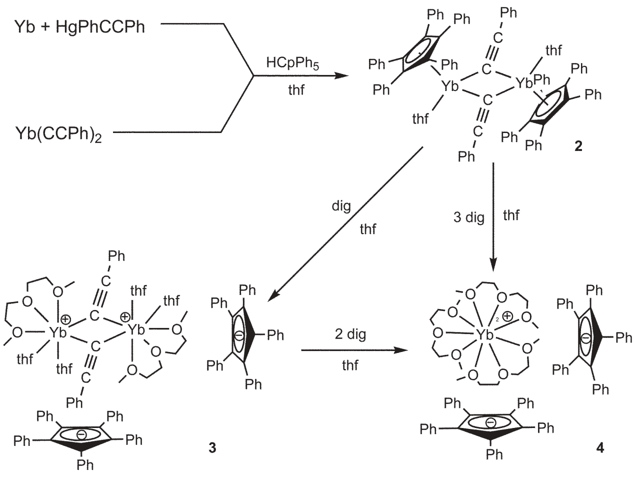

Scheme 1

f^n-organometallics and without structural validation.[10] Reaction of HCpPh$_5$ with a thf solution of Yb(C≡CPh)$_2$, or reaction of Yb metal, HgPh(C≡CPh) (generating YbPh(C≡CPh) *in situ*), and HCpPh$_5$ in thf gave red [Yb(CpPh$_5$)(μ-C≡CPh)(thf)]$_2$ (**2**) (Scheme 1).‡

Complex **2** is dimeric as established by X-ray crystallography§ (Fig. 2) and the IR spectrum showed a weak *ν*(C≡C) absorption at 2033 cm^{-1}. Each Yb is six-coordinate, being bound to two bridging PhC≡C ligands, an η^5-CpPh$_5$ ligand and one coordinated thf. In contrast, seven-coordinate [EuCp*(μ-C≡CPh)(thf)$_2$]$_2$ has an additional coordinated thf per metal.[5] The Yb–C(C≡CPh) distances are comparable to those of seven-coordinate [YbI(μ-C≡CPh)(dme)]$_2$ (Yb–C 2.584(7), 2.602(8) Å)[11] after allowance for differences due to coordination number.[12] The structure of **2** also features long Yb–C(CpPh$_5$) distances (<Yb–C> 2.726 Å *cf.* 2.652 Å for six-coordinate [YbCp*{Si(SiMe$_3$)$_3$}(thf)$_2$][13]) reflecting ligand bulk, and a highly distorted pseudo-tetrahedral Yb geometry (cent–Yb–X 118.1–124.6°, cent = centroid of CpPh$_5$, X = O or C, *cf.* X–Yb–X 89.2(2)–97.4(2)°).

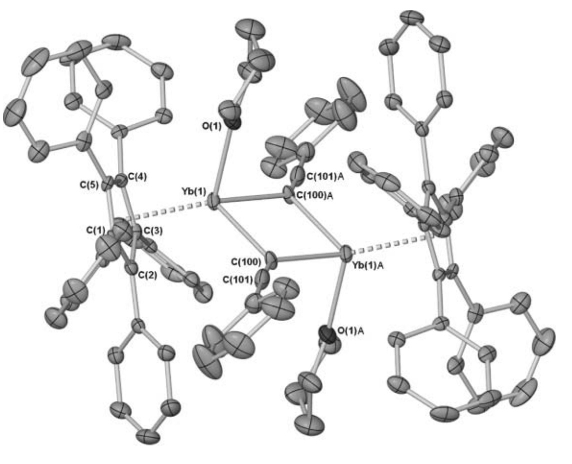

Fig. 2 The molecular structure of centrosymmetric **2** shown with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Yb–C(CpPh$_5$) 2.713(6)–2.740(6), Yb(1)–C(100) 2.522(6), Yb(1)–C(100)^A 2.542(6), Yb–O(1) 2.371(5); Yb–C–C 129.5(5), 139.7(5). ^{A} denotes atoms at (2 − *x*, 2 − *y*, 1 − *z*).

Once isolated, **2** could not be redissolved in thf, but dropwise addition of other neutral donors such as dme (1,2-dimethoxyethane) or dig to the thf suspension gave clear red to yellow solutions. In contrast, attempted dissolution of **2** in the above pure solvents caused rapid precipitation of yellow solids. On a preparative scale, careful addition of dig to **2** in thf gave a red solution which ultimately yielded large red crystals of [Yb(μ-C≡CPh)(dig)(thf)$_2$]$_2$[CpPh$_5$]$_2$·4thf (**3**) (Scheme 1) along with a minor amount of smaller green–yellow crystals of the ion pair [Yb(dig)$_3$][CpPh$_5$]$_2$ (**4**).‡ Treatment of **3** with excess dig in thf also gave **4** as a green–yellow precipitate (Scheme 1). Thus the use of near stoichiometric amounts of diglyme is critical to the isolation of **3** (and presumably also **1**). NMR characterisation of **3** in D$_8$-thf was consistent with the composition established by X-ray crystallography (see below) and the *ν*(C≡C) absorption was observed by Raman spectroscopy. A ^{171}Yb NMR signal was not observed for **3** whereas **4** has a sharp peak at 241 ppm, consistent with that observed for the [Yb(thf)$_6$]$^{2+}$ dication (256 ppm).[14] The structure of **4** is predicted to be a solvent separated ion pair based on the known [Yb(dig)$_3$]$^{2+}$ dication.[15]

The structure of the dication of **3**§ (Fig. 3) is similar to that of **1**, having a Ln$_2$(μ-C≡CPh)$_2$ core, but in **3** the co-ligands are one diglyme and two thf ligands giving a coordination number of seven, one less than for the larger[12] Eu^{2+} in **1**. The geometry at Yb can be described as distorted pentagonal bipyramidal (in Fig. 3, O(4) and C(1)$^\#$ are axial, O–Yb–C 170.46(9)°). The unit cell contains two independent, but centrosymmetric, dications differing only in the bridging phenylacetylide arrangement. One dication has near equivalent Yb–C distances and Yb–C–C angles whereas the other (Fig. 3) is considerably distorted. The Yb–C distances (Fig. 3) for the more symmetrical phenylacetylide bridge are very close to those of seven-coordinate [YbI(μ-C≡CPh)(dme)]$_2$.[11] However, for the unsymmetrical bridge one Yb–C bond is longer (Yb(1)$^\#$–C(1) 2.662(3) Å) and also there is a close approach of the PhC≡C β-carbon to the associated Yb atom (Yb(1)–C(2)

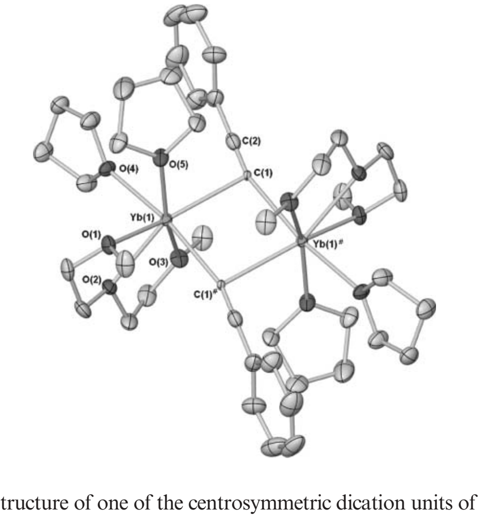

Fig. 3 Structure of one of the centrosymmetric dication units of **3** shown with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) [values in parentheses refer to the second independent dication]: Yb(1)–C(1) 2.662(3), Yb(1)–C(1)$^\#$ 2.586(3) [Yb(2)–C(58) 2.587(3), Yb(2)–C(58)* 2.600(3)], Yb–O 2.463(2)–2.579(2) [2.447(3)–2.530(2)]; Yb–C–C 163.4(3), 102.3(3) [132.2(3), 135.5(3)]. $^\#$Atoms at (1 − *x*, −*y*, 1 − *z*); *Atoms at (−*x*, 1 − *y*, −*z*).

3.130(4) Å). The $CpPh_5^-$ anions in **3** are not bound to the metal but reside in the crystal lattice. Each dication is surrounded on four sides by the face of a $CpPh_5^-$ anion generating a honeycomb network of anions with chains of cations located within the channels. A similar pattern is also observed in **1** but is less regular. An analogous 3-D arrangement of cations and anions has been described for Group 2 complexes with elongated dinuclear dications *e.g.* $[CaBr(thf)_4]_2^{2+}$ or $[MgMe(pmdta)]_2^{2+}$.[16]

The complexes **1** and **3** represent a new class of organolanthanoid(II) cations and their stability appears dependent upon the choice of co-ligands and counter ions, and they provide support for the proposal that $[Ln^{III}(L)(C{\equiv}CR)(S)]_2^{2+}$ moieties are present in organolanthanoid(III) catalysed *cis*-selective linear dimerisation of alkynes.[17]

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Notes and references

‡ *Syntheses*: **1**: Dropwise addition of $P{\equiv}CBu^t$ (600 μL, 3.7 mmol) to a solution of $Eu(C{\equiv}CPh)_2$ (3.0 mmol) in thf (10 mL) at −30 °C and warming to room temperature followed by concentration, addition of PhMe and diglyme and cooling to −30 °C gave an inhomogeneous mixture (0.17 g) containing a few yellow crystals. Mp 145–148 °C. IR (Nujol/cm^{-1}): 1654m, 1508m, 1378m, 1261m, 1090m, 856w, 801w, 696w, 674w. MS (ES+, *m*/*z*) 253 (85%, $Eu_2(C{\equiv}CPh)_2^{2+}$), 864 (90, $Eu_2C_2(dig)_4^+$). **2**: (a) $Yb(C{\equiv}CPh)_2$ (2.0 mmol) in thf (40 ml) was stirred with $HCpPh_5$ (0.88 g, 2.0 mmol) at room temperature for 24 h, then at 50 °C for 2 h. Filtration and concentration of the filtrate gave a red solid which was washed with warm thf (60 ml) and dried under vacuum giving crystalline red **2** (0.48 g, 30%). (b) Excess Yb metal (1.04 g, 6.0 mmol), $HgPh(C{\equiv}CPh)$ (0.76 g, 2.0 mmol) and $HCpPh_5$ (0.88 g, 2.0 mmol) in thf (50 mL) were stirred at room temperature for 24 h. Filtration and concentration of the filtrate gave **2** as a red crystalline solid (1.12 g, 70%). Anal. Found for $C_{94}H_{76}O_2Yb_2$: C 69.9, H 5.2, Yb 22.5. Calc. C 71.2, H 4.8, Yb 22.0%. IR (Nujol/cm^{-1}): 2033w ($\nu(C{\equiv}C)$), 1594m, 1500s, 1178w, 1142w, 1073m, 1022m, 911m, 866m, 802w, 778m, 758m, 739m, 702s. **3**: Dropwise addition of diglyme (0.1 mL 0.7 mmol) to a suspension of **2** (0.39 g, 0.25 mmol) in thf (40 mL) followed by filtration, concentration of the filtrate and standing gave large red blocks of **3** mixed with a few smaller green–yellow crystals of **4**. The red crystals were separated by hand (0.46 g, 80%). Anal. Found for $C_{130}H_{152}O_{14}Yb_2$: C 66.9, H 6.3, Yb 15.8. Calc. C 68.3, H 6.7, Yb 15.2%. IR (Nujol/cm^{-1}): (Raman, 2034w, $\nu(C{\equiv}C)$), 1588s, 1498s, 1282w, 1246w, 1173w, 1141m, 1072m, 1050m, 1026m, 909m, 868m, 802m, 776m, 759w, 738m, 701s. ^1H NMR (400 MHz, 293 K, D_8-thf) δ/ppm: 6.70–6.60, br m, 60H, Ph; 3.62, m, 32H, thf; 3.48, s, 12H, $C\mathit{H}_3O$; 3.30, s, 16H, $C\mathit{H}_2O$; 1.77, m, 32H, thf. ^{13}C NMR (100.6 MHz, 293 K, D_8-thf) δ/ppm: 26.4, 68.3, 71.1, 72.9, 121.3, 121.8, 123.6, 124.9, 126.9, 127.9, 132.7, 132.9, 138.6, 144.1. **4**: Excess diglyme (0.5 ml, 3.5 mmol) was added to **3** (0.18 g, 0.08 mmol) in thf (5 ml) giving a green–yellow precipitate of **4** (0.09 g, 80%). Anal. Found for $C_{88}H_{92}O_9Yb$: C 72.9, H 5.8, Yb 11.6. Calc. C 72.1, H 6.3, Yb 11.8%. IR (Nujol/cm^{-1}): 1589s, 1498s, 1278w, 1249w, 1172w, 1142m, 1090m, 1045m, 996w, 945w, 910w, 868m, 802m, 776m, 739m, 710s, 701s. ^1H NMR (400 MHz, 293 K, D_8-thf) δ/ppm: 6.77–6.69, br m, 50H, Ph; 3.46, s, 18H, $C\mathit{H}_3O$; 3.28, s, 24H, $C\mathit{H}_2O$. ^{13}C NMR (100.6 MHz, 293 K, D_8-thf) δ/ppm: 71.1, 72.9, 121.3, 121.8, 127.0, 132.8, 143.9. ^{171}Yb NMR (52.5 MHz, 293 K, thf) δ/ppm: 241, $\Delta\nu_{1/2}$ = 20 Hz.

§ *Crystal data*: **1**: $C_{79}H_{133}Eu_2O_{113.5}P_4$, M = 1726.65, triclinic, $P\bar{1}$ (no. 2), a = 14.945(3), b = 16.865(3), c = 18.374(4) Å, α = 72.77(3), β = 88.65(3), γ = 79.01(3)°, V = 4340(2) $Å^3$, Z = 2, D_c = 1.321 g cm^{-3}, μ = 1.561 mm^{-1}, 15127 unique data (R_{int} = 0.085) converged to $R1$ = 0.101, wR_2 = 0.150 ($R1$ = 0.170, wR_2 = 0.171 all data). **2**: $C_{94}H_{76}O_2Yb_2$, M = 1583.72, triclinic, $P\bar{1}$ (no. 2), a = 12.4427(2), b = 13.1004(1), c = 13.3179(2) Å, α = 116.42(1), β = 99.74(1), γ = 102.07(1)°, V = 1814.0(6) $Å^3$, Z = 1, D_c = 1.450 g cm^{-3}, μ = 2.613 mm^{-1}, 8749 unique data (R_{int} = 0.084) converged to $R1$ = 0.055, wR_2 = 0.123 ($R1$ = 0.082, wR_2 = 0.132 all data). **3**: $C_{130}H_{152}O_{14}Yb_2$ M = 2284.60, monoclinic, $P2_1/c$ (no. 14), a = 25.9306(2), b = 22.2060(2), c = 20.6683(1) Å, β = 111.4124(3)°, V = 11080(4) $Å^3$, Z = 4, D_c = 1.370 g cm^{-3}, μ = 1.74 mm^{-1}, 27101 unique data (R_{int} = 0.072) converged to $R1$ = 0.041, wR_2 = 0.083 ($R1$ = 0.075, wR_2 = 0.095 all data). CCDC 286665–286667. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514358f

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