

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

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General procedures: All manipulations were carried out under inert atmosphere using standard Schlenk, vacuum line, and dry box techniques. Solvents were dried from the appropriate drying agent and degassed by distillation under nitrogen. Microanalyses were performed by the Campbell Microanalytical Laboratories, University of Otago, New Zealand. Difficulties with accurate elemental analyses of CpPh₅ compounds were observed as has been noted previously.^[1] IR spectra are for Nujol mulls on NaCl plates using a Perkin Elmer 1600 FTIR. ¹H and ¹³C NMR spectra were obtained using a Bruker 400 MHz spectrometer. ¹⁷¹Yb NMR spectra were recorded on a Bruker 300 MHz spectrometer and referenced to external 0.15M Yb(C₅Me₅)₂ in thf/10%C₆D₆. D₈-thf was dried and distilled from Na/K alloy under nitrogen prior to use. ³¹P NMR spectra of reaction mixtures were obtained using a Bruker 300 MHz spectrometer, and were referenced to external 85% H₃PO₄ in D₂O. ES mass spectra were recorded using a VG Fisons Platform 2 spectrometer, MALDI-TOF mass spectra were obtained on a Fisons VG ToFSpec using a Nitrogen UV laser (337 nm). Thf solutions of Yb(C≡CPh)₂,^[2] and Eu(C≡CPh)₂,^[3] were prepared *in situ* from excess Ln and Hg(CCPPh)₂. P≡CBu^t,^[4] and HCpPh₅,^[5] were prepared by literature methods. HgPh(C≡CPh) was prepared by a modified literature procedure^[6] from HgPhCl, HC≡CPh and NaOH in 60% aq. Bu^tOH and characterised spectroscopically: M.p. 95-

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97 °C (lit.^[7] 95 °C). IR (Nujol/cm⁻¹): 2133w, 1647w, 1631w, 1593w, 1570w, 1210w, 1069w, 1023w, 908w, 841w, 796m, 753s, 727s, 690s. MS (ES+, *m/z*): 380, (M⁺).

Syntheses: **[Eu(CCPPh)(dig)₂]₂[P₂C₃Bu^t₃]₂ (1)**: A solution of Eu(C≡CPh)₂ (3.0 mmol) in thf (10 ml) was cooled to -30 °C and P≡CBu^t (600 μl, 3.7 mmol) was added dropwise and the mixture was warmed to room temperature. The ³¹P NMR spectrum of this solution showed numerous peaks, the major resonances being observed as broad peaks at δ = 261, 214, and 91 ppm. Reduction of the solvent volume and addition of PhMe until formation of a precipitate, followed by addition of diglyme until a homogeneous solution was obtained, and cooling to -30 °C gave an inhomogeneous material containing yellow crystals of **1** (0.17 g, 34%). Mp. 145-148 °C. IR (Nujol/cm⁻¹): 1654m, 1508m, 1378m, 1261m, 1090m, 856w, 801w, 696w, 674w. MS (ES+, *m/z*) 253 (85%, Eu₂(CCPh)₂²⁺), 864 (90, Eu₂C₂(dig)₄⁺).

Reaction of Yb(C≡CPh)₂ with P≡CBu^t: A solution of Yb(C≡CPh)₂ (3.0 mmol) in thf (20 ml) was cooled to -30 °C and P≡CBu^t (480 μl, 3.0 mmol) was added dropwise and the mixture was warmed to room temperature. The ³¹P NMR spectrum of this solution showed numerous peaks, the major resonances being observed as broad peaks at 263, 236, 192 ppm. Several attempts to isolate a tractable material from this mixture were unsuccessful. However, after addition of diglyme, colourless crystals of the pentaphosphorus cage compound P₅C₅Bu^t₅ were obtained.

[Yb(CpPh₅)(CCPh)(thf)]₂ (2): (a) A solution of Yb(C≡CPh)₂ (2.0 mmol) in thf (40 ml) was stirred with HCpPh₅ (0.88 g, 2.0 mmol) at room temperature for 24h, then at 50 °C for 2h. Filtration and concentration of the filtrate gave a red solid suspended in

a brown solution. The solution was decanted and the product 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≡CPh) (0.76 g, 2.0 mmol) and HCpPh₅ (0.88 g, 2.0 mmol) in thf (50 ml) were stirred at room temperature for 24h. Filtration and concentration of the filtrate gave a red solid suspended in a brown solution. The mixture was heated for 24h then the solvent was decanted leaving crystalline red **2** (1.12 g, 70%). Anal. Found for C₉₄H₇₆O₂Yb₂: C 69.9, H 5.2, Yb 22.5. Calc. C 71.2, H 4.8, Yb 22.0%. IR (Nujol/cm⁻¹): 2033w, 1594m, 1500s, 1178w, 1142w, 1073m, 1022m, 911m, 866m, 802w, 778m, 758m, 739m, 702s.

[Yb(CCPPh)(dig)(thf)₂]₂[CpPh₅]₂·4thf (3): Diglyme (*ca.* 0.1 ml 0.7 mmol) was added drop-wise to a suspension of **2** (0.39 g, 0.25 mmol) in thf (40 ml) until a dark red solution was obtained. Filtration, concentration of the filtrate, and standing gave large red blocks of **3** mixed with a few smaller green-yellow crystals of **4** (IR identification). The red crystals of **3** were separated by hand and dried briefly under nitrogen (0.48 g, 80%). A portion of the sample was further recrystallised from thf for analytical and spectroscopic analyses. Anal. Found for C₁₃₀H₁₅₂O₁₄Yb₂: 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, ν(C≡C)), 1588s, 1498s, 1282w, 1246w, 1173w, 1141m, 1072m, 1050m, 1026m, 909m, 868m, 802m, 776m, 759w, 738m, 701s. ¹H NMR (400 MHz, 293K, D₈-thf) δ/ppm: 6.70-6.60, br m, 60H, Ph; 3.62, m, 32H, thf; 3.48, s, 12H CH₃O, 3.30, s, 16H, CH₂O; 1.77, m, 32H, thf. ¹³C NMR (100.6 MHz, 293K, D₈-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.

[Yb(dig)₃][CpPh₅]₂ (4): Excess diglyme (0.5 ml, 3.5 mmol) was added to a solution of **3** (0.18 g, 0.08 mmol) in thf (5 ml) giving a green-yellow precipitate in a pale red solution. The precipitate was collected by filtration and dried under vacuum giving green-yellow **4** (0.09 g, 80%). Anal. Found for C₈₈H₉₂O₉Yb: 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, 293K, D₈-thf) δ/ppm: 6.77-6.69, br m, 50H, Ph; 3.46, s, 18H CH₃O, 3.28, s, 24H, CH₂O. ¹³C NMR (100.6 MHz, 293K, D₈-thf) δ/ppm: 71.1, 72.9, 121.3, 121.8, 127.0, 132.8, 143.9. ¹⁷¹Yb NMR (52.5 MHz, 293K, thf) δ/ppm: 241, Δν_{1/2} = 20Hz.

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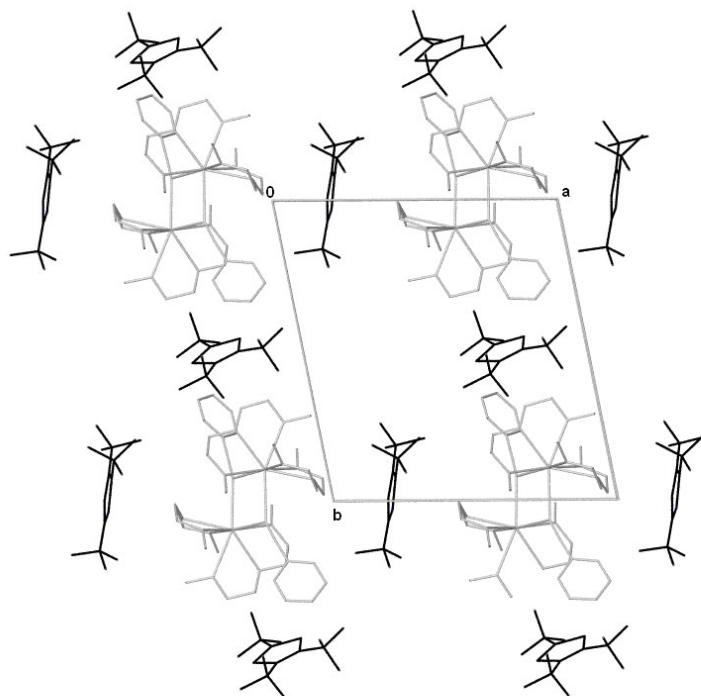


Fig. S1. Stick representation of **1**, viewed down the *c*-axis and showing the $[\text{Eu}(\text{CCPh})(\text{dig})_2]_2^{2+}$ di-cations surrounded by four $\text{P}_2\text{C}_3(\text{Bu}^t)_3^-$ anions.

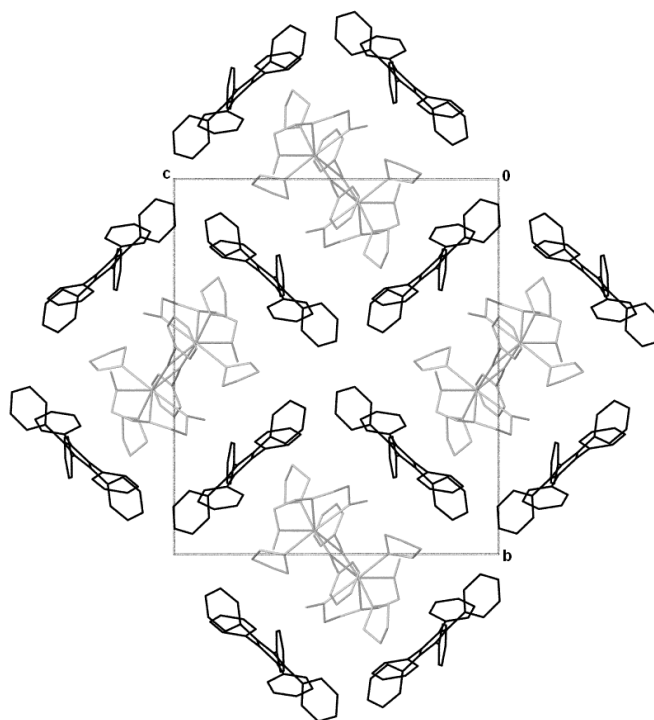


Fig. S2. Stick representation of **3**, viewed down the *a*-axis and showing the [Yb(CCPh)(dig)(thf)₂]₂²⁺ di-cations (grey) lying in channels formed by the faces of four CpPh₅⁻ anions (black); lattice thf molecules have been omitted for clarity