Reaction of $M(C_5Me_5)_2(OEt_2)$, M = Eu or Yb, with Phenylacetylene; Formation of Mixed-valence $Yb_3(C_5Me_5)_4(\mu\text{-}C{\equiv}CPh)_4$ and $Eu_2(C_5Me_5)_2(\mu\text{-}C{\equiv}CPh)_2$(tetrahydrofuran)$_4$

James M. Boncella, T. Don Tilley, and Richard A. Andersen*

Chemistry Department and Materials and Molecular Research Division of Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, U.S.A.

Reaction of $Yb(C_5Me_5)_2(OEt_2)$ with $PhC{\equiv}CH$ yields the mixed-valence complex $Yb_3(C_5Me_5)_4(\mu\text{-}C{\equiv}CPh)_4$ though $Eu(C_5Me_5)_2(OEt_2)$ reacts with $PhC{\equiv}CH$ to give the divalent complex $Eu_2(C_5Me_5)_2(\mu\text{-}C{\equiv}CPh)_2(thf)_4$ (thf = tetrahydrofuran) after crystallization from thf.

The divalent metallocene, $Yb(C_5Me_5)_2(OEt_2)$, is a single-electron-transfer reagent towards transition metal carbonyls and inorganic molecules.[1] To explore the scope of the electron-transfer properties of this divalent metallocene, we have examined some of its reactions with organic molecules.

The complex, $Yb(C_5Me_5)_2(OEt_2)$, does not react with CO (18 atm, 20 °C) nor with $PhC{\equiv}CPh$ (refluxing toluene), but it does react with $PhC{\equiv}CH$ (3 : 4 molar ratio, toluene, 20 °C) to give red needles from toluene (−10 °C, 52% yield, m.p. 275—278 °C) of $Yb_3(C_5Me_5)_4(C{\equiv}CPh)_4$,† ^1H n.m.r. (C_6D_6, 26 °C) δ 3.49 (s, 60 H, $w_{\frac{1}{2}}$ 25 Hz), 10.6 (s, 4 H, $w_{\frac{1}{2}}$ 20 Hz), 12.7 (s, 8 H, $w_{\frac{1}{2}}$ 20 Hz), and 25.5 (s, 8 H, $w_{\frac{1}{2}}$ 20 Hz); i.r. (Nujol) $\nu(C{\equiv}C)$ 2040 cm^{-1}.

An ORTEP diagram is shown in Figure 1. The crystal used in the *X*-ray study was grown from benzene solution and the

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† All new compounds gave satisfactory elemental analyses.

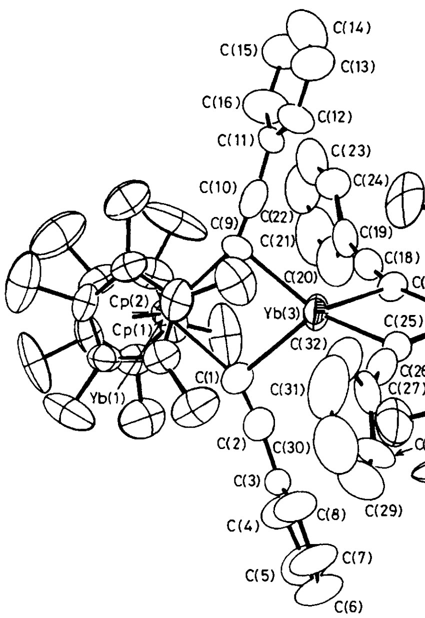

Figure 1. ORTEP Diagram of $Yb_3(C_5Me_5)_4(\mu\text{-}C{\equiv}CPh)_4$. Cp = C_5Me_5. Some distances (Å) and angles (°) are: Yb–centroid (av.) 2.33; C≡C (av.) 1.22(1); C–C(Ph) (av.) 1.47(1); Yb(1)–C(1)–Yb(3) 97.6(2); Yb(1)–C(9)–Yb(3) 95.6(2); Yb(2)–C(17)–Yb(3) 96.8(2); Yb(2)–C(25)–Yb(3) 95.9(2); C(1)–Yb(1)–C(9) 86.0(2); C(1)–Yb(3)–C(9) 80.3(2); C(17)–Yb(3)–C(25) 81.4(2); C(17)–Yb(2)–C(25) 85.9(2); C(1)–Yb(3)–C(25) 113.9(2); C(9)–Yb(3)–C(17) 113.6(2).

complex contains a molecule of benzene of solvation. *Crystal data:* $C_{78}H_{86}Yb_3$, M = 1548.68, monoclinic, space group $P2_1/c$, a = 18.388(3), b = 13.598(1), c = 26.852(3) Å, β = 90.92(1)°, U = 6712.9 Å^3, D_c = 1.526 g cm^{-3}, Mo-K_α radiation, λ = 0.71073 Å, μ(Mo-K_α) = 41.73 cm^{-1}. The structure was solved by a combination of MULTAN and Fourier methods and refined using 5715 unique reflections [$F^2 > 3\sigma(F^2)$] measured on a CAD4 diffractometer ($2\theta_{max}$ 45°). The current R value is 0.0327.‡

The averaged Yb–C (C_5Me_5) bond length is 2.61(2) Å. This value is in the range found for related trivalent $Yb(C_5Me_5)_2$ complexes whose co-ordination numbers are identical to the terminal ytterbium atoms in the phenylacetylide (2.57—2.65 Å)[1,2] and significantly shorter than that found, 2.742(7) Å, in the divalent complex of identical co-ordination number of $Yb(C_5Me_5)_2(pyridine)_2$.[3] The averaged Yb(1,2)–C (C≡CPh) bond length is 2.40(2) Å and the averaged Yb(3)–C (C≡CPh) bond length is 2.52(1) Å. The bond length data support the idea that Yb(1,2) are trivalent and Yb(3) is divalent, since Shannon suggests that the radius of Yb^{III} is 0.16 Å smaller than Yb^{II}.[4] Thus, $Yb_3(C_5Me_5)_4(\mu\text{-}C{\equiv}CPh)_4$ is a Yb^{III,II,III} mixed-valence complex of idealized D_{2d} symmetry. Magnetic susceptibility studies, μ_{eff} (5—30 K, per Yb^{III}) = 3.58 ± 0.04 μ_B and μ_{eff} (90—300 K, per Yb^{III}) = 4.53 ± 0.01 μ_B, show that the complex is a class I or trapped valence complex, *i.e.,* there is no electron exchange between the Yb^{III} centres.[5]

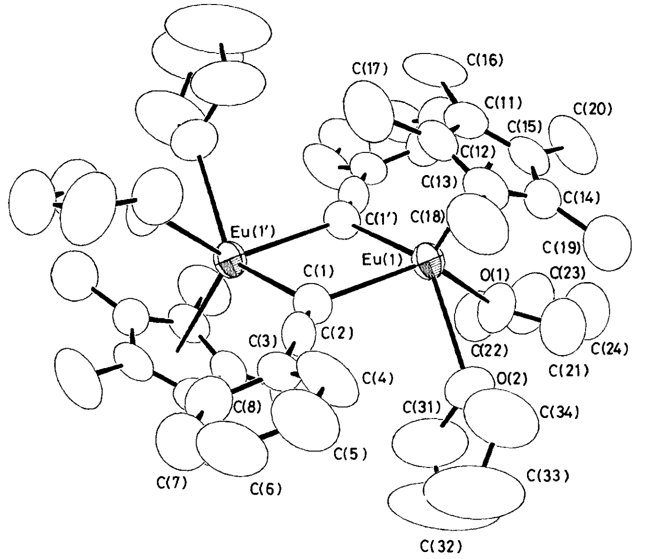

Figure 2. ORTEP Diagram of $Eu_2(C_5Me_5)_2(\mu\text{-}C{\equiv}CPh)_2(thf)_4$. Some distances (Å) and angles (°) are: Eu–centroid 2.55; C≡C 1.188(8); C–C (Ph) 1.44(1); centroid–Eu–C (C≡CPh) (av.) 113.2; centroid–Eu–O (av.) 112.4; O(1)–Eu(1)–C(1') 86.6(2); O(2)–Eu(1)–C(1) 80.4(2); O(1)–Eu(1)–C(1) 135.5(2); O(2)–Eu(1)–C(1') 132.2(2); C(1)–Eu(1)–C(1') 84.6(2); Eu(1)–C(1)–Eu(1') 95.4(2).

The co-ordination number of the central ytterbium atom is four and the geometry is distorted tetrahedral. The dihedral angle formed by the intersection of the planes defined by Yb(3)C(1)C(9) and Yb(3)C(17)C(25) is 65.4°. A higher co-ordination number of Yb(3), created by interaction with the β-carbon atoms of the bridging phenylacetylide ligand [the Yb(3)–C(2,10,18,26) distances vary from 3.01—3.26 Å], is prevented by the close approach of one of the *ortho*-carbon atoms of each phenyl ring to the methyl carbon atoms of the C_5Me_5 ligand. This contact distance ranges from 3.26—3.60 Å. The compact geometry produces considerable asymmetry in the bridging phenylacetylide carbon angles; the averaged Yb(3)–C(1,9,17,25)–C(2,10,18,26) and Yb(1,2)–C(1,9,17,25)–C(2,10,18,26) angles are 107(4) and 156(3)°, respectively.

Reaction of the divalent europium metallocene, $Eu(C_5Me_5)_2(OEt_2)$[6], with PhC≡CH takes a different course, since the product $Eu_2(C_5Me_5)_2(C{\equiv}CPh)_2(thf)_4$† (thf = tetrahydrofuran) (orange prisms from thf, −10 °C, 47% yield, ν(C≡C) 2025 cm^{-1}) is based upon divalent europium, and the acetylene is acting as a protic acid only. An ORTEP diagram is shown in Figure 2. *Crystal data:* $C_{52}H_{72}Eu_2O_4$, M = 1065.07, orthorhombic, space group *Pbca,* a = 17.251(3), b = 15.445(2), c = 18.732(2) Å, U = 4991.1 Å^3, Z = 4, D_c = 1.417 g cm^{-3}, Mo-K_α radiation, λ = 0.71073 Å, μ(Mo-K_α) = 25.33 cm^{-1}. The structure was solved by a combination of Patterson and Fourier methods and refined using 1744 unique reflections [$F^2 > 3\sigma(F^2)$] measured on a Nonius CAD4 diffractometer ($2\theta_{max}$ 45°). The current R value is 0.0264.‡

The averaged Eu–C(C_5Me_5) distance is 2.82(2) Å, similar to that found [2.795(7) Å] in $Eu(C_5Me_5)_2(OEt_2)$.[6] The averaged Eu–O (thf) distance of 2.62(1) Å is similar to that [2.594(4) Å] found in $Eu(C_5Me_5)_2(OEt_2)$. The bridging phenylacetylide is slightly asymmetric; the Eu–C(1,1') distances of 2.709(7) and 2.702(7) Å are identical though the Eu(1)C(1)C(2) and Eu(1')C(1)C(2) angles are 129.1(6) and 135.5(6)°, respectively.

The geometry of the bridging phenylacetylide groups in the divalent and mixed-valence derivatives is similar to that found in the trivalent samarium complex, $Sm_2(C_5H_4Me)_4(\mu\text{-}C{\equiv}CPh)_2$.[7]

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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