Title

REACTION OF M(C5Me5)2(OEt2),M = Eu OR Yb, WITH PHENYLRCETYLENE; FORMATION OF MIXED-VALENCE Yb3(C5Me5)4(u-=CPh)4 AND Eu2(C5Me5)2(u-C=CPH)2(thf)4

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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 $Eu_2(C_5Me_5)_2(\mu\text{-}C{\equiv}CPh)_2(thf)_4$

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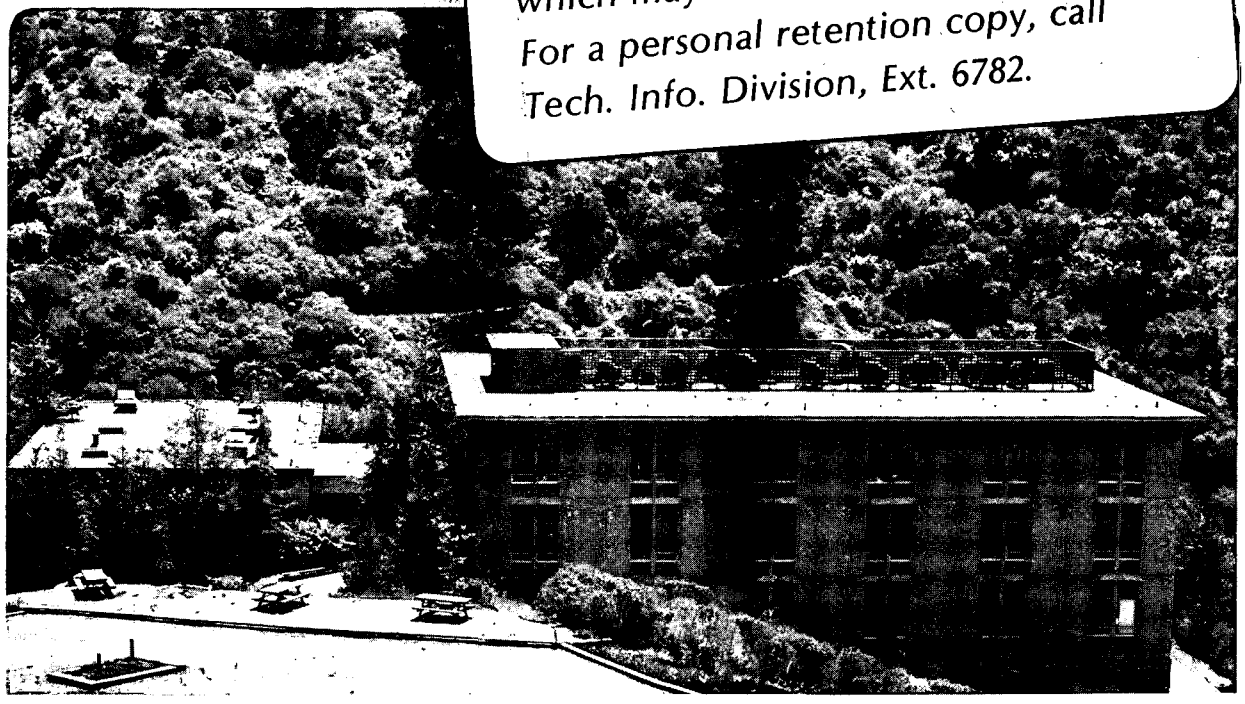

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LBL-17335

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 $Eu_2(C_5Me_5)_2(\mu\text{-}C{\equiv}CPh)_2(thf)_4$.

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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 $Eu_2(C_5Me_5)_2(\mu\text{-}C{\equiv}CPh)_2(thf)_4$ after crystallization from tetrahydrofuran.

The divalent metallocene, $Yb(C_5Me_5)_2(OEt_2)$, is a single electron-transfer reagent towards transition metal carbonyls and inorganic molecules.[1] In order 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≡CPh (refluxing toluene), but it does react with PhC≡CH (3:4 molar ratio, toluene, 20°C) to give red needles from toluene (-10°C, 52% yield, m.p. 275-278°C) of $Yb_3(C_5Me_5)_4(C{\equiv}Ph)_4$,† ^1H n.m.r. (C_6D_6, 26°C) δ 3.49 (s, 60 H, $\nu\frac{1}{2}$ = 25 Hz), 10.6 (s, 4 H, $\nu\frac{1}{2}$ = 20 Hz), 12.7 (s, 8 H, $\nu\frac{1}{2}$ = 20 Hz), 25.5 (s, 8 H, $\nu\frac{1}{2}$ = 20 Hz), and i.r. (Nujol) ν(C≡C) = 2040 cm^{-1}.

An ORTEP diagram is shown in Figure I. The crystal used in the X-ray study was grown from benzene solution and the 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)°, V = 6712.9Å^3, Dc = 1.526 gcm^{-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 coordination numbers are identical to the terminal ytterbium atoms in the phenylacetylide

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† All new compounds gave satisfactory elemental analyses.

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

(2.57-2.65Å) [1,2] and significantly shorter than that found, 2.742(7) Å, in the divalent complex of identical coordination number of $Yb(C_5Me_5)_2(py)_2$.[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 0.16Å smaller than Yb(II).[4] Thus, $Yb_3(C_5Me_5)_4$-$(\mu\text{-}C{\equiv}Ph)_4$ is a Yb(III,II,III) mixed-valence complex of idealized D_{2d} symmetry. Magnetic susceptibility studies, μ_{eff} [5-30K, per Yb(III)] = 3.58 ±0.04 B.M. and μ_{eff} [90-300K, per Yb(III)] = 4.53 ±0.01 B.M., show that the complex is a class I or trapped valence complex, i.e., there is no electron exchange between the Yb(III) centers.[5]

The coordination 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 coordination number of Yb(3), created by interaction with the β-carbon atoms of the bridging phenylacetlide ligand [the Yb(3) C(2,10,18,26) distances vary from 3.01 to 3.26Å], 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 to 3.60Å. 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 $Eu_2(C_5Me_5)_2(C{\equiv}CPh)_2(thf)_4^{\dagger}$ (orange prisms from thf, -10°C, 47% yield, $\nu(C{\equiv}C)$ = 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 II. Crystal Data: $C_{52}H_{72}Eu_2O_4$, M = 1065.07,

orthorhombic, space group P_{bca}, a = 17.251(3), b = 15.445(2), c = 18.732(2)Å, U = 4991.1Å, Z = 4, D_c = 1.417 g cm^{-3}, MoK_α radiation, λ = 0.71073Å, $\mu(MoK_\alpha)$ = 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) anagles are 129.1(6) and 135.5(6)°, respectively.

The geometry of the bridging phenylacetlide 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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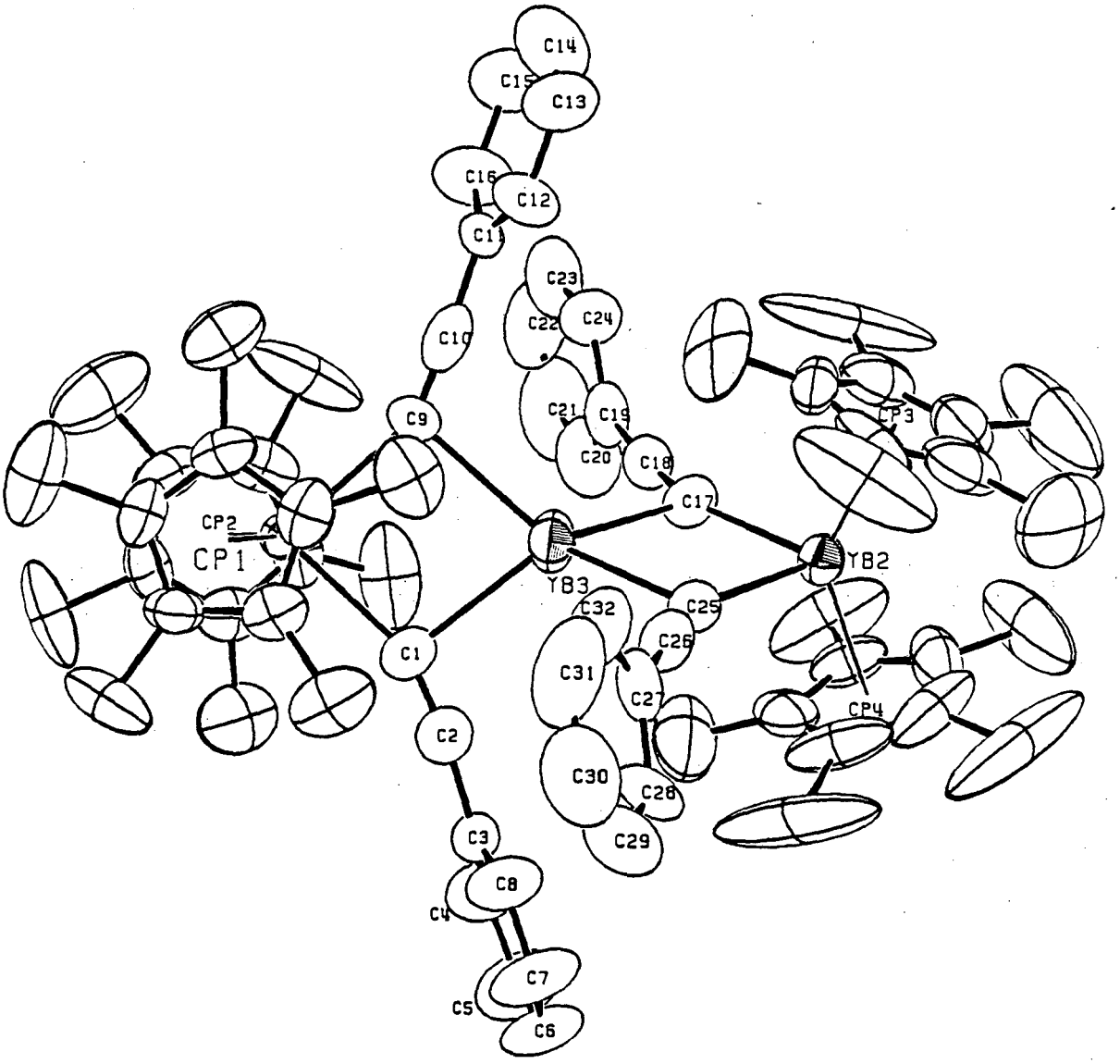

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Figure 1

FIGURE I. ORTEP Diagram of $Yb_3(C_5Me_5)_4(\mu\text{-}C{\equiv}CPh)_4$. Some distances and angles are:

Yb-centroid (ave.)	= 2.33 Å
C≡C (ave.)	= 1.22(1) Å
C-C(Ph) (ave.)	= 1.47(1) Å
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)°

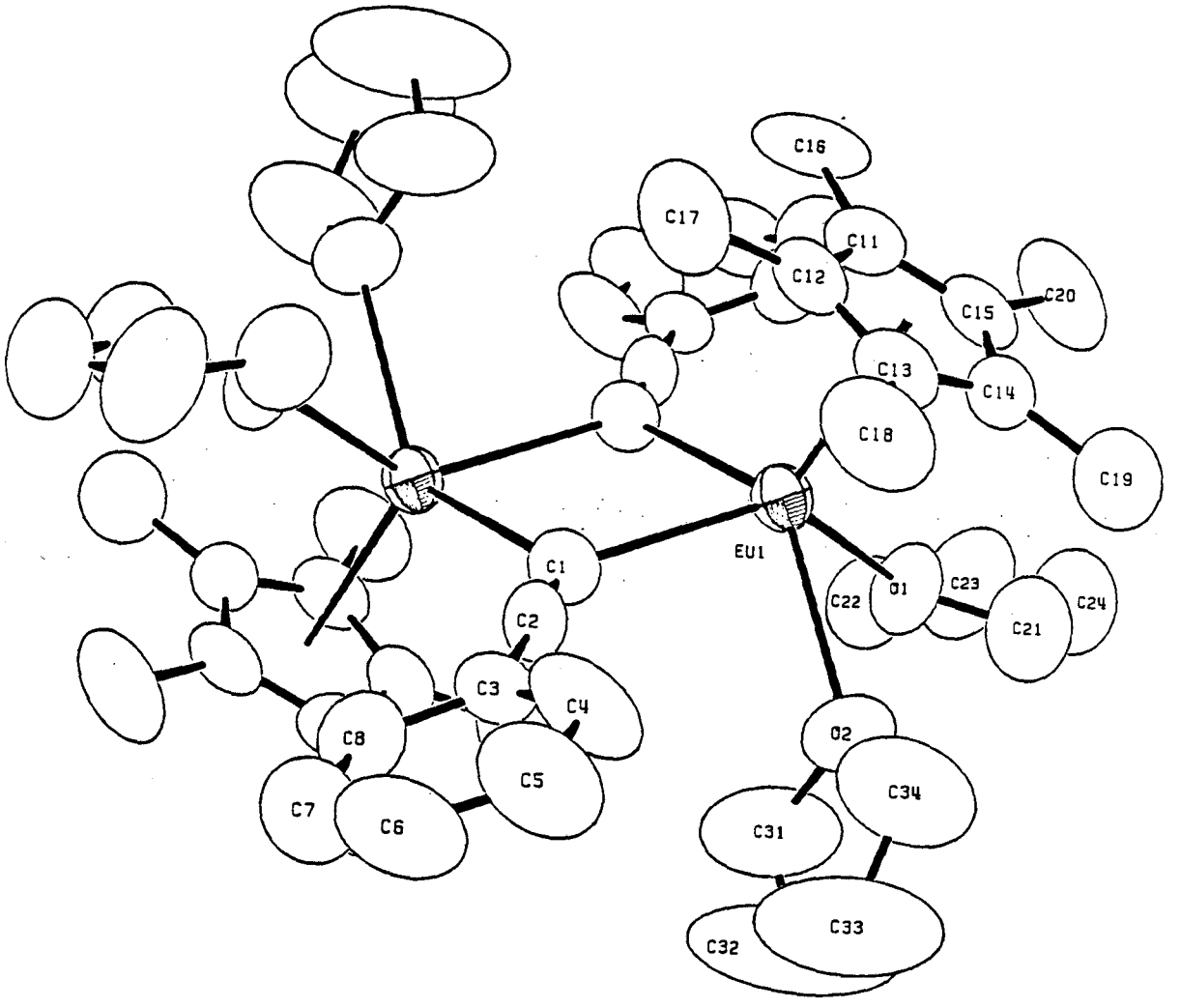
C16
C17
C11
C12
C15
C20
C13
C14
C18
C19
EU1
C1
C2
O1
C23
C22
C24
C21
C3
C4
C8
O2
C5
C34
C7
C6
C31
C33
C32
XBL 832-8246

Figure II

FIGURE II. ORTEP Diagram of $Eu_2(C_5Me_5)_2(\mu\text{-}C{\equiv}CPh)_2(thf)_4$. Some distances and angles are:

Eu-centroid	= 2.55 Å
C≡C	= 1.188(8) Å
C-C(Ph)	= 1.44(1) Å
Centroid-Eu-C(C≡CPh) (ave.)	= 113.2°
Centroid-Eu-O (ave.)	= 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)°

Positional Parameters for $Yb_3(C_5Me_5)_4(\mu\text{-}C{\equiv}CPh)_4$

Atom	x	y	z	Atom	x	y	z
YB1	Ø.13852(2)	Ø.1713Ø(3)	Ø.14861(1)	C24	Ø.3941(7)	Ø.4799(9)	Ø.1614(4)
YB2	Ø.36922(2)	Ø.32421(4)	Ø.36Ø64(1)	C25	Ø.2523(5)	Ø.2443(7)	Ø.3486(3)
YB3	Ø.251Ø9(3)	Ø.25422(4)	Ø.25425(2)	C26	Ø.1969(5)	Ø.2Ø82(8)	Ø.3645(3)
C1	Ø.21Ø7(5)	Ø.Ø986(8)	Ø.212Ø(3)	C27	Ø.1319(5)	Ø.1663(8)	Ø.3873(3)
C2	Ø.232Ø(5)	Ø.Ø323(8)	Ø.24Ø1(3)	C28	Ø.1361(6)	Ø.Ø752(7)	Ø.4113(4)
C3	Ø.25ØØ(5)	-Ø.Ø544(7)	Ø.2711(4)	C29	Ø.Ø746(6)	Ø.Ø341(9)	Ø.433Ø(4)
C4	Ø.3Ø9Ø(7)	-Ø.1135(9)	Ø.2597(4)	C3Ø	Ø.Ø1Ø1(7)	Ø.Ø851(11)	Ø.4279(5)
C5	Ø.3278(8)	-Ø.192Ø(1Ø)	Ø.2915(5)	C31	Ø.ØØ46(7)	Ø.1695(13)	Ø.4Ø51(5)
C6	Ø.2886(7)	-Ø.2149(9)	Ø.3318(4)	C32	Ø.Ø657(6)	Ø.211Ø(1Ø)	Ø.3846(4)
C7	Ø.2334(7)	-Ø.1556(9)	Ø.3414(4)	C4Ø	Ø.Ø371(5)	Ø.213Ø(9)	Ø.2119(4)
C8	Ø.2144(6)	-Ø.Ø781(8)	Ø.3136(4)	C41	Ø.Ø395(5)	Ø.1122(8)	Ø.2127(4)
C9	Ø.1832(5)	Ø.3263(7)	Ø.1799(4)	C42	Ø.Ø163(5)	Ø.Ø786(7)	Ø.165Ø(4)
C1Ø	Ø.1831(5)	Ø.4147(9)	Ø.1831(3)	C43	-Ø.ØØ34(5)	Ø.1585(9)	Ø.1364(4)
C11	Ø.1791(5)	Ø.5243(7)	Ø.1842(4)	C44	Ø.Ø1Ø2(5)	Ø.2414(8)	Ø.1654(4)
C12	Ø.1421(6)	Ø.5711(8)	Ø.2223(4)	C45	Ø.Ø541(6)	Ø.Ø5Ø2(1Ø)	Ø.2566(5)
C13	Ø.1379(6)	Ø.6728(9)	Ø.2249(5)	C46	Ø.ØØ16(7)	-Ø.Ø263(9)	Ø.1522(6)
C14	Ø.1722(8)	Ø.7262(11)	Ø.19Ø7(6)	C47	-Ø.Ø479(7)	Ø.1612(14)	Ø.Ø878(5)
C15	Ø.2Ø81(8)	Ø.6825(1Ø)	Ø.1537(5)	C48	-Ø.ØØ58(6)	Ø.3494(1Ø)	Ø.1497(5)
C16	Ø.2131(7)	Ø.5787(9)	Ø.1491(5)	C49	Ø.Ø516(6)	Ø.28Ø6(1Ø)	Ø.2566(4)
C17	Ø.3727(5)	Ø.3334(8)	Ø.271Ø(3)	C5Ø	Ø.2566(5)	Ø.1475(9)	Ø.Ø975(4)
C18	Ø.3915(5)	Ø.3556(8)	Ø.2291(3)	C51	Ø.2159(6)	Ø.Ø636(8)	Ø.Ø9ØØ(4)
C19	Ø.4183(5)	Ø.3875(9)	Ø.1811(3)	C52	Ø.1538(6)	Ø.Ø859(8)	Ø.Ø626(3)
C2Ø	Ø.4669(7)	Ø.3357(11)	Ø.1559(5)	C53	Ø.1558(6)	Ø.1853(9)	Ø.Ø532(4)
C21	Ø.4938(7)	Ø.371Ø(14)	Ø.1112(5)	C54	Ø.2195(7)	Ø.2219(9)	Ø.Ø742(4)
C22	Ø.4675(8)	Ø.4541(13)	Ø.Ø918(5)	C55	Ø.1ØØ1(8)	Ø.Ø1Ø8(11)	Ø.Ø397(5)
C23	Ø.4199(8)	Ø.5Ø8Ø(11)	Ø.117Ø(5)	C56	Ø.1Ø67(9)	Ø.2426(13)	Ø.Ø189(5)

Positional Parameters for $Yb_3(C_5Me_5)_4(\mu\text{-}C{\equiv}CPh)_4$

Continued

Atom	x	y	z
C57	Ø.2494(1Ø)	Ø.3242(1Ø)	Ø.ØØ75(6)
C58	Ø.33Ø7(7)	Ø.15Ø2(14)	Ø.1234(5)
C59	Ø.2381(8)	-Ø.ØØ385(11)	Ø.1Ø63(5)
C6Ø	Ø.376Ø(7)	Ø.5148(9)	Ø.3539(4)
C61	Ø.4Ø21(7)	Ø.4976(9)	Ø.4ØØ2(5)
C62	Ø.3484(8)	Ø.4612(9)	Ø.429Ø(5)
C63	Ø.2837(6)	Ø.4538(8)	Ø.4Ø29(5)
C64	Ø.2954(7)	Ø.4893(8)	Ø.354Ø(4)
C65	Ø.4116(12)	Ø.5615(1Ø)	Ø.31Ø3(6)
C66	Ø.4779(9)	Ø.5325(14)	Ø.4194(9)
C67	Ø.3612(14)	Ø.4423(15)	Ø.4872(6)
C68	Ø.2163(8)	Ø.42Ø5(12)	Ø.4331(7)
C69	Ø.2314(9)	Ø.4918(12)	Ø.32Ø1(7)
C7Ø	Ø.4948(6)	Ø.2598(9)	Ø.3958(5)
C71	Ø.4886(5)	Ø.2261(9)	Ø.348Ø(4)
C72	Ø.4322(6)	Ø.1576(8)	Ø.3451(5)
C73	Ø.4Ø61(6)	Ø.15Ø7(1Ø)	Ø.3928(5)
C74	Ø.4437(7)	Ø.2157(11)	Ø.423Ø(4)
C75	Ø.4337(12)	Ø.2129(15)	Ø.4791(6)
C76	Ø.351Ø(8)	Ø.Ø7Ø7(11)	Ø.4Ø63(8)
C77	Ø.4156(9)	Ø.Ø964(11)	Ø.2985(6)
C78	Ø.5452(7)	Ø.2545(14)	Ø.3Ø45(6)
C79	Ø.5557(7)	Ø.3221(12)	Ø.4181(8)
C8Ø	Ø.7655(1Ø)	Ø.2167(13)	Ø.ØØ26(6)
C81	Ø.6927(1Ø)	Ø.2376(13)	Ø.ØØ3Ø7(5)
C82	Ø.6688(1Ø)	Ø.3348(14)	Ø.ØØ16Ø(6)
C83	Ø.72ØØ(9)	Ø.3993(12)	-Ø.ØØ41(5)
C84	Ø.7852(11)	Ø.3672(15)	-Ø.ØØ1Ø6(6)
C85	Ø.8Ø66(1Ø)	Ø.2743(16)	Ø.ØØ3Ø(6)

Positional Parameters for $Eu(C_5Me_5)_2(\mu\text{-}C{\equiv}CPh)_2(thf)_4$

Atom	x	y	z
EU1	Ø.ØØ3Ø1(2)	Ø.Ø5139(3)	Ø.Ø98Ø4(2)
O1	Ø.1Ø8Ø(3)	Ø.1693(4)	Ø.12Ø3(4)
O2	-Ø.Ø71Ø(4)	Ø.2Ø11(4)	Ø.Ø99Ø(4)
C1	Ø.1Ø39(5)	-Ø.Ø198(5)	Ø.ØØ46(5)
C2	Ø.1717(5)	-Ø.Ø311(5)	Ø.Ø1Ø8(4)
C3	Ø.254Ø(4)	-Ø.Ø43Ø(5)	Ø.Ø188(4)
C4	Ø.3Ø11(5)	-Ø.Ø597(7)	-Ø.Ø369(6)
C5	Ø.383Ø(6)	-Ø.Ø7Ø3(8)	-Ø.Ø264(6)
C6	Ø.4116(6)	-Ø.Ø611(7)	Ø.Ø393(7)
C7	Ø.3663(6)	-Ø.Ø463(7)	Ø.Ø964(6)
C8	Ø.2875(5)	-Ø.Ø354(7)	Ø.Ø854(5)
C11	Ø.Ø288(5)	-Ø.Ø894(6)	Ø.1925(5)
C12	-Ø.Ø488(5)	-Ø.Ø938(6)	Ø.1729(5)
C13	-Ø.Ø885(4)	-Ø.Ø239(6)	Ø.2Ø53(5)
C14	-Ø.Ø335(5)	Ø.Ø258(6)	Ø.2426(5)
C15	Ø.Ø377(5)	-Ø.Ø148(6)	Ø.2352(4)
C16	Ø.Ø937(6)	-Ø.1531(7)	Ø.1716(6)
C17	-Ø.Ø828(7)	-Ø.1651(8)	Ø.129Ø(6)
C18	-Ø.1746(5)	-Ø.ØØ86(8)	Ø.2Ø13(6)
C19	-Ø.Ø489(7)	Ø.1Ø36(8)	Ø.2873(6)
C2Ø	Ø.1137(6)	Ø.ØØ99(9)	Ø.2698(6)
C21	Ø.11Ø1(6)	Ø.2279(8)	Ø.1788(6)
C22	Ø.1763(6)	Ø.1882(7)	Ø.Ø792(6)
C23	Ø.2359(6)	Ø.2156(9)	Ø.1281(8)
C24	Ø.1962(6)	Ø.2448(8)	Ø.1935(7)
C31	-Ø.Ø636(8)	Ø.251Ø(9)	Ø.Ø338(8)
C32	-Ø.12Ø8(7)	Ø.3148(9)	Ø.Ø34(1)
C33	-Ø.1719(8)	Ø.293(1)	Ø.Ø83(1)
C34	-Ø.1389(8)	Ø.23Ø(1)	Ø.1331(8)

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