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Synthesis and structure of ytterbium(II) complexes with the tetraphenylethylene dianion

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Ytterbium(II) and ytterbium(III) halides react with disodium or dipotassium tetraphenylethenide to form the complex dianion $[Yb(Ph_2CCPh_2)_2]^{2-}$, which demonstrates bis-η^3-coordination of the tetraphenylethylene dianions to the Yb^{2+} cation in a solid state.

The tetraphenylethylene dianion is a well-known[1–3] but virtually unexplored ligand in transition metal chemistry. Previously, we reported the synthesis and structure of yttrium and lutetium complexes with the tetraphenylethylene dianion.[4,5] The complexes revealed an unusual bis-η^3-coordination of the $[Ph_4C_2]^{2-}$ dianion to the M^{3+} cation in the solid state. To investigate the synthetic potential of the dianionic tetraphenylethenide ligand in the organometallic chemistry of lanthanides(II), we examined the reactions of $K_2[Ph_2CCPh_2]$ and $Na_2[Ph_2CCPh_2]$ with ytterbium halides.

The reaction of dipotassium- or disodiumtetraphenylethylene with YbI_2 or $YbCl_2$ leads to homoleptic *ate*-complexes **1** and **2**.§ Both **1** and **2** are extremely sensitive to water and oxygen traces, but they can be stored for prolonged time in sealed evacuated vessels.

$$YbHal_2 + 2M_2[Ph_2CCPh_2] \rightarrow M_2[Yb(Ph_2CCPh_2)_2](THF)_n + 2MHal\downarrow$$

Hal = I, M = K **1** $n = 8$
Hal = Cl, M = Na **2** $n = 7$

Since the reduction potential of tetraphenylethylene to the dianion is much higher than that of the Yb^{3+}/Yb^{2+} transition,¶ complex **2** can also be generated from $YbCl_3$:††

$$YbCl_3 + 2.5\,Na_2[Ph_2CCPh_2] \rightarrow Na_2[Yb(Ph_2CCPh_2)_2](THF)_7 + 0.5\,Ph_4C_2 + 3\,NaCl\downarrow$$

2

In contrast to the *ate*-complexes of yttrium[4] and lutetium,[5] where the absorption band of $(Ph_2CCPh_2)^{2-}$ was strongly shifted to a short-wavelength region by 80–90 nm, compared to alkali metal salts (λ_{max} = 485 nm),[10] such a shift was not observed in the UV-VIS spectra of complexes **1** (λ_{max} = 495 nm, THF) and **2** (475 nm, THF).

Diglyme decomposes compounds **1** and **2** to give an insoluble light-red precipitate and a solution containing a mixture of dipotassium or disodium tetraphenylethylene. The recrystallization of **1** from dimethoxyethane (DME) leads to dipotassium tetraphenylethylene, which crystallises as dark-cherry needles, and a light-red precipitate almost insoluble in DME and THF. Perhaps, there is an equilibrium between the complex dianion $[Yb(Ph_4C_2)_2]^{2-}$ and the 'free' dianion of tetraphenylethylene, and a neutral ytterbium complex in *n*-electron donor solvents due to solvation effects:

$$[Yb(Ph_4C_2)_2]^{2-} \rightleftharpoons [Yb(Ph_4C_2)] + [Ph_4C_2]^{2-}.$$

The NMR spectra of **1** and **2** point out to the dynamic processes caused by the equilibrium between 'free' and coordinated

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§ All synthetic operations were carried out in evacuated and sealed Schlenk-type vessels. 1.454 g (2.15 mmol) of $YbI_2(THF)_{3.5}$ was added to a solution of $K_2[Ph_4C_2]$ in 60 ml of THF, obtained from 1.474 g (4.43 mmol) of $Ph_2C{=}CPh_2$. The mixture was stirred for 2 h at room temperature and then refluxed for 10 h. The solvent was removed, the resulting precipitate was extracted with hot THF (60 ml), the resulting dark-red solid was recrystallised from THF and dried in vacuum. 2.379 g (1.59 mmol, 74%) of crystalline solid soluble in THF and poorly soluble in 1,4-dioxane was obtained. Found: Yb, 11.44%, calc. for $K_2[Yb(Ph_2CCPh_2)_2]\cdot 8THF$: 11.59%. UV-VIS (THF) λ_{max}/nm: 370, 495. ^1H NMR (250 MHz, [$^2H_8$]THF) δ: 5.78 (br. m, 4H), 6.59 (br. m, 8H), 6.99 (br. m, 8H).

¶ The reduction potential of Yb^{3+} to Yb^{2+} lies between –1.10 V[6] and –1.15 V[7] in water, and equals to –1.52 V[8] for the couple $YbCp_3/YbCp_3^-$ in THF. The reduction potential of Ph_4C_2 to $[Ph_4C_2]^{2-}$ is –2.47 V in THF.[9]

†† The solution of $Na_2[Ph_4C_2]$ in 170 ml of THF, obtained from 4.907 g (14.8 mmol) of $Ph_2C{=}CPh_2$, was added to 1.650 g (5.91 mmol) of anhydrous $YbCl_3$. The mixture was stirred for two days and refluxed for four days. The solvent was evaporated. The black-cherry precipitate was twice extracted with hot THF (160 ml), washed with THF and diethyl ether, dried, recrystallised from hot THF and dried in vacuum. The product was obtained as dark-cherry microcrystalline powder (5.016 g, 4.54 mmol, 77%). Found: Yb, 15.67%; calc. for $Na_2[Yb(Ph_2CCPh_2)_2](THF)_3$, 15.73%. Since the crystalline product loses significant amount of THF while vacuum drying, the powder composition does not correspond to the single-crystal composition of **2**. UV-VIS (THF) λ_{max}/nm: 365, 475. ^1H NMR (250 MHz, [$^2H_8$]THF) δ: 5.88 (br. m, 4H), 6.61 (br. m, 8H), 6.88 (br. m, 8H).

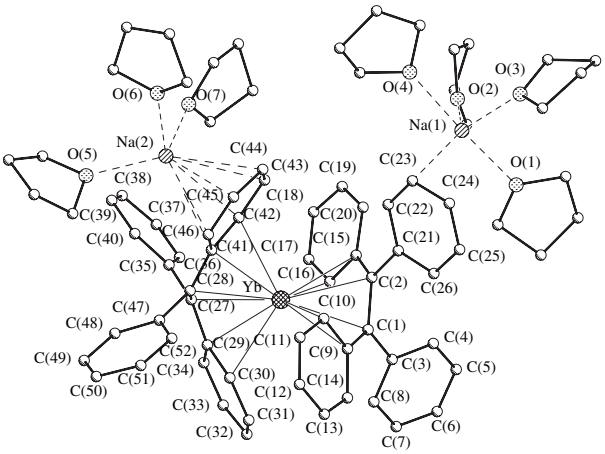

Figure 1 The general view of $[Na(THF)_3][Na(THF)_4][Yb(Ph_2CCPh_2)_2]$ **2**. Selected bond lengths (Å): Yb–C(1) 2.618(5), Yb–C(2) 2.652(5), Yb–C(9) 2.700(6), Yb–C(10) 2.659(5), Yb–C(15) 2.740(6), Yb–C(16) 2.632(5), Yb–C(27) 2.668(5), Yb–C(28) 2.671(5), Yb–C(29) 2.750(4), Yb–C(41) 2.698(4), Yb–C(30) 2.672(5), Yb–C(42) 2.642(5), C(1)–C(2) 1.493(6), C(1)–C(9) 1.412(8), C(2)–C(15) 1.423(8), C(9)–C(10) 1.455(7), C(9)–C(14) 1.437(8), C(10)–C(11) 1.385(8), C(11)–C(12) 1.355(8), C(12)–C(13) 1.388(8), C(13)–C(14) 1.345(8), C(15)–C(16) 1.460(7), C(15)–C(20) 1.419(8), C(16)–C(17) 1.383(8), C(17)–C(18) 1.372(8), C(18)–C(19) 1.390(8), C(19)–C(20) 1.376(8), C(27)–C(28) 1.503(6), C(27)–C(29) 1.438(7), C(28)–C(41) 1.404(7), C(29)–C(34) 1.450(7), C(29)–C(30) 1.426(8), C(30)–C(31) 1.381(7), C(31)–C(32) 1.369(7), C(32)–C(33) 1.382(8), C(33)–C(34) 1.380(7), C(41)–C(42) 1.455(8), C(42)–C(43) 1.401(7), C(43)–C(44) 1.378(7), C(44)–C(45) 1.399(8), C(45)–C(46) 1.371(7), C(41)–C(46) 1.456(7). A range for C–C bond lengths for uncoordinated phenyl rings: C(3)–C(8) 1.355(8)–1.402(7), C(21)–C(26) 1.374(7)–1.410(7), C(35)–C(40) 1.373(7)–1.413(7), C(47)–C(52) 1.350(9)–1.406(7).

dianions. However, a complicated character of the equilibrium makes the NMR spectra of **1** and **2** nearly uninformative. In order to obtain structural information on the complexes, we carried out the X-ray structure determination of **2**.[‡‡]

Complex **2** consists of the dianion $[Yb(Ph_4C_2)_2]^{2-}$ and two sodium cations coordinated to four and three THF molecules, Na(1) and Na(2), respectively. Na(1) is bounded to one carbon atom C(23) with a distance of 2.960(6) Å, whereas Na(2) is bounded to six carbon atoms C(41)–C(46) of a ligand phenyl ring with the Na(2)–C distances of 2.789(5) through 3.018(6) Å. Coordination of tetraphenylethylene dianions with Yb^{2+} in $[Yb(Ph_4C_2)_2]^{2-}$ is similar to that in $[Na(THF)_6][Y(Ph_4C_2)_2](THF)_2$ **3**[4] and $[Na(diglyme)_2][Lu(Ph_4C_2)_2](THF)_{0.5}$ **4**.[5] There are 12 short contacts Yb–C in $[Yb(Ph_4C_2)_2]^{2-}$ (six per ligand) with the carbon atoms C(1), C(2), C(27) and C(28) ($C'_{=}$), *ipso*-carbon atoms C(9), C(15), C(29), C(41) (C'_{ipso}) and *ortho*-carbon atoms C(10), C(16), C(30), C(42) (C'_{ortho}) of tetraphenylethenide phenyl rings.[§§]

The redistribution of C–C bond lengths inside phenyl rings coordinated to Yb^{2+} and also elongation of the former tetraphenylethylene double bond[11,12] up to 1.498(6) Å (average) point out that the tetraphenylethylene dianion coordinated to Yb^{2+} has a bis-η^3-allyl-like bonding type,[5] where an excessive electron density is located dominantly not only at the former double bond atoms ($C'_{=}$) but also at the coordinated *ortho*-carbon atoms (C'_{ortho}). All the Yb–C bonds in **2** are somewhat elongated, compared with analogous M–C bonds in **3** and **4**, due to the higher Yb^{2+} ionic radius. Taking into account differences among Y^{3+}, Lu^{3+} and Yb^{2+} ionic radii (for CN=8 r_{Ln} = 1.159, 1.117 and 1.28 Å, respectively),[13] note that analogous averaged M–C distances in **3** and **4** are nearly identical. The Yb–C distances extrapolated from Y and Lu complexes (**3** and **4**) structural data should be about 2.63–2.64 (Yb–$C_{=}$), 2.78–2.80 (Yb–C_{ipso}) and 2.73 Å (Yb–C_{ortho}). However, the averaged Yb–C_{ipso} and Yb–C_{ortho} bond lengths found in **2** are

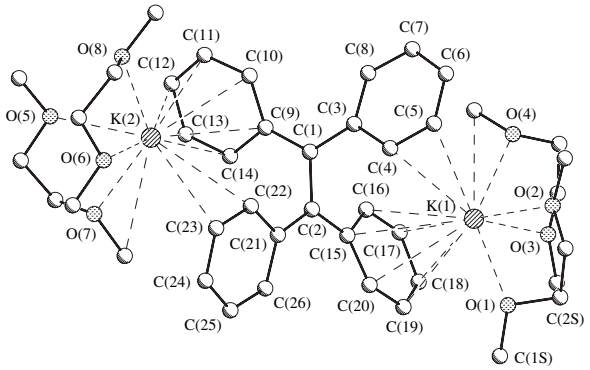

Figure 2 The general view of $[K(DME)_2]_2[Ph_2CCPh_2]$ **6**. Selected bond lengths (Å): C(1)–C(9) 1.425(2), C(1)–C(3) 1.435(2), C(1)–C(2) 1.497(2), C(2)–C(15) 1.435(2), C(2)–C(21) 1.436(2), C(3)–C(8) 1.426(2), C(3)–C(4) 1.427(2), C(4)–C(5) 1.384(2), C(5)–C(6) 1.388(3), C(6)–C(7) 1.395(3), C(7)–C(8) 1.384(2), C(9)–C(10) 1.435(2), C(9)–C(14) 1.437(2), C(10)–C(11) 1.383(2), C(11)–C(12) 1.394(3), C(12)–C(13) 1.397(3), C(13)–C(14) 1.384(3), C(15)–C(20) 1.424(2), C(15)–C(16) 1.432(2), C(16)–C(17) 1.380(2), C(17)–C(18) 1.391(3), C(18)–C(19) 1.386(3), C(19)–C(20) 1.389(2), C(21)–C(26) 1.429(2), C(21)–C(22) 1.430(2), C(22)–C(23) 1.381(2), C(23)–C(24) 1.394(3), C(24)–C(25) 1.396(2), C(25)–C(26) 1.382(2).

shorter by 0.06–0.08 Å (2.72 and 2.65 Å, respectively). This discrepancy is, probably, due to the larger ionic radius of Yb^{2+}, allowing more effective interaction with the *ipso* and *ortho* positions of phenyl rings.

The structural parameters of **2** can be compared with alkali metal salts of the tetraphenylethylene dianion: $\{Na[Na(Et_2O)_2(Ph_4C_2)]\}_\infty$ **5**,[1] $[K(DME)_2]_2[Ph_2CCPh_2]$ **6**, whose structure

[‡‡] Numerous attempts to recrystallise **1** from THF or 1,4-dioxane did not lead to crystals acceptable for X-ray structure determination. However, the recrystallization of **2** from THF at room temperature afforded crystals suitable for X-ray studies. Crystals of **6** were obtained by reaction of $Ph_2C{=}CPh_2$ with potassium mirror in THF, followed by recrystallization from DME. Crystals of **2** ($C_{80}H_{96}Na_2O_7Yb$, M = 1388.59) are orthorhombic, space group *Fdd*2, at 120 K: a = 39.306(3), b = 56.131(4), c = 12.2594(9) Å, V = 27048(3) Å^3, Z = 16 (Z' = 1), d_{calc} = 1.354 g cm^{-3}, μ(MoKα) = 14.52 cm^{-1}, F(000) = 11584. Intensities of 34437 reflections were measured with a Smart 1000 CCD diffractometer [λ(MoKα) = = 0.71072 Å, ω-scans, $2\theta < 57°$] and 14493 independent reflections (R_{int} = 0.0588) were used in a further refinement.

Crystals of **6** ($C_{42}H_{60}K_2O_8$, M = 771.10) are monoclinic, space group $P2_1/c$, at 100 K: a = 13.922(2), b = 19.671(3), c = 15.476(3) Å, β = = 94.398(8)°, V = 4226(1) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.212 g cm^{-3}, μ(MoKα) = 2.73 cm^{-1}, F(000) = 1656. Intensities of 23996 reflections were measured with a Smart APEX II CCD diffractometer [μ(MoKα) = = 0.71072 Å, ω-scans, $2\theta < 58°$] and 11108 independent reflections (R_{int} = = 0.0446) were used in further refinement. Both structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The positions of hydrogen atoms were calculated geometrically. The refinement converged to wR_2 = 0.0691 and GOF = 0.910 for all independent reflections [R_1 = = 0.0407 was calculated against F for 10107 observed reflections with $I > 2\sigma(I)$] for **2** and to wR_2 = 0.1005 and GOF = 1.028 for all independent reflections [R_1 = 0.0428 was calculated against F for 7108 observed reflections with $I > 2\sigma(I)$] for **6**. All calculations were performed using the SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 637864 and 637865 for compounds **2** and **6**, respectively. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2007.

[§§] Carbon atoms coordinated with Yb^{2+} are labeled with an apostrophe: $C'_{=}$, C'_{ipso} and C'_{ortho}.

was determined in this work, and $[Cs(diglyme)]_2[Ph_4C_2]$ **7**.[3] In **5**, one of the sodium cations is η^6-bound to the dianion, resembling the bis-η^3-allyl type of bonding. The redistribution of C–C bond lengths in the dianion of **5** demonstrates that a negative charge is mainly localised at the former double bond carbon atoms and at every *ortho* positions of all phenyl rings. The structure of **7** is similar to that of **6** with the exception that the cesium cation is η^3-bound to one diglyme molecule in **7**. Compound **6** contains two potassium cations η^2-coordinated to two DME molecules, η^6- and η^2-coordinated with two different phenyl rings with K···C interatomic separation within the range 3.077(2)–3.412(2) Å. The elongation of the former double bond[11,12] to 1.496(2) Å and an almost identical redistribution of C–C bond lengths in all phenyl rings in **6** indicate a more or less uniform localization of an excessive negative charge in all of the four phenyl rings, like in **5**.

The synthetic potential of the tetraphenylethenide ligand in 4*f*-organometallic chemistry has been extended to the field of Ln^{2+} complexes. The effect of this ligand environment on the reaction chemistry of Yb^{2+} compounds is under investigation.

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