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Synthesis and structure of triphenylmethyl derivatives of ytterbium $[Yb(THF)_6]^{2+}[Ph_3C]_2^-$ and $[(THF)_4Yb(\mu\text{-}Cl)_2Yb(THF)_4]^{2+}$ $[Ph_3Cl]_2^-$

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Abstract

Ionic triphenylmethyl complexes of ytterbium $[Yb(THF)_6]^{2+}[Ph_3C]_2^-$ (**1**) and $[(THF)_4Yb(\mu\text{-}Cl)_2Yb(THF)_4]^{2+}[Ph_3C]_2^-$ (**2**) have been synthesized by the reaction of Ph_3CCl with ytterbium in THF. Complex **1** has also been prepared by the reaction of ytterbium with a dimer of triphenylmethyl radicals in THF. It was found that this reaction was catalyzed by ytterbium dihalides.

According to X-ray diffraction result the crystal structures of **1** and **2** are composed of isolated ions. The $[Yb(THF)_6]^{2+}$ cation has an ideal octahedral coordination of the central Yb atom with the Yb–O distance of 2.390(7) Å. The $[(THF)_4Yb(\mu\text{-}Cl)_2\text{-}Yb(THF)_4]^{2+}$ cation is a centrosymmetrical dimer in which each Yb atom is bonded to four oxygen atoms of THF molecules and two $(THF)_4Yb$ units are linked via two symmetrical μ-Cl bridges, both Yb–Cl distances being 2.715(4) Å. The $[Ph_3C]^-$ anion in **1** and **2** has a propeller-type geometry with the planar environment of the central carbon atom (within 0.02 Å in **1** and 0.006 Å in **2**). The Ph rings are rotated out of the average CC_3 plane of the central fragment of $[Ph_3C]^-$ anion by 28.2° in **1** and by 26.6, 31.9, 33.7° in **2**.

Keywords: Ytterbium; Lanthanide complexes; Carbanions; Triphenylmethyl derivatives; X-ray diffraction

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1. Introduction

Samarium, europium and ytterbium are known to react readily with alkyl- and arylhalides to give Grignard-type complexes RLnI [1–3]. Recently we have found that similar reactions of Yb with Ph_3ECl (E = Si, Ge, Sn) in THF at room temperature lead to formation of organo-silicon, -germanium and -tin complexes $(Ph_3E)_2Yb(THF)_4$ in high yields [4–6]. In the present paper we report the results of our investigations of the reactions of Yb with Ph_3CCl, which is the carbon analogue of triphenylsilicon, -germanium, and -tin chlorides.

Earlier it has been shown [7,8] that Nd, Pr, Gd and Ho react with Ph_3CCl in THF to give red-brown solutions containing complexes of the Ph_3CLnCl_2 and $(Ph_3C)_2LnCl$ types. Their formation was established by analysis of products of hydrolysis of the reaction mixture. These complexes are believed to have carbon–lanthanoid bonds [7,8].

2. Results and discussion

We have found that ytterbium reacts readily with Ph_3CCl in THF at room temperature without any activation. The following consecutive changes were observed on stirring of the reaction mixture. Initially (after ca. 1 h) a white precipitate was formed and the solution became pale-yellow. After that the solution instantaneously turned red. On subsequent stirring the red colouring gradually became more and more deep; simultaneously the precipitate dissolved slowly. The course of this and all other reactions with metallic Yb was periodically monitored by measuring consumption of Yb and by visual observation.

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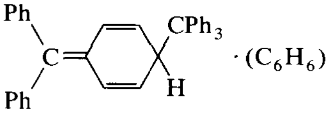
It was found that in the initial stages of the reaction, before the appearance of a red colour in the solution, the consumption of Yb amounted to 0.5 mol per mole of starting Ph_3CCl. The reaction mixture at that moment contained $YbCl_2(THF)_2$ and $Ph_3C\cdot$ radicals in equilibrium with the dimer. Ytterbium dichloride was isolated at this stage in 52.9% yield. The equilibrium mixture of triphenylmethyl radicals and its dimer (after separation from $YbCl_2(THF)_2$ for identification) was oxidized by dry air in benzene to $Ph_3COOCPh_3$ which was isolated in 84.3% yield (relative to starting Ph_3CCl).

At the following stages, after ca. 3 h of stirring of the reagents, 1 mol of Yb was consumed in the reaction. However, even 15 h of further stirring of reaction mixture did not result in any additional consumption of Yb. The reaction mixture after ca. 3 h from the beginning of the reaction contained compounds **1**, **2** and $YbCl_2(THF)_2$. Both triphenylmethyl salts **1** and **2** were isolated as individual crystalline solids and identified by X-ray analysis.

After 15 h of stirring the only product was complex **2** which was isolated in 87.7% yield.

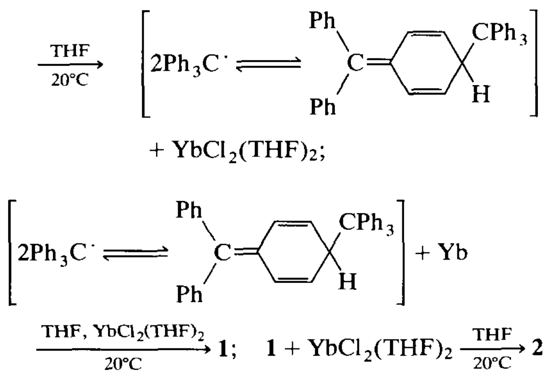
It should be noted that in benzene Yb reacts with Ph_3CCl much more slowly (over ca. 200 h) and gives in high yields only $YbCl_2$ and the dimer of triphenylmethyl radicals. X-ray study of the compound has been carried out, to show that the dimer of triphenylmethyl radicals isolated in the crystalline state from the reaction of Yb with Ph_3CCl in benzene has a previously known 1-diphenylmethylene-4-triphenylmethylcyclohexa-2,5-diene structure [9–11] but also contains a solvate benzene molecule



Full structural details for this compound will be published elsewhere.

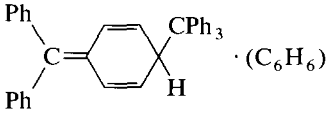
Thus, the general scheme of the reaction of Yb with Ph_3CCl in THF can be presented as follows:

$2Ph_3CCl + Yb$



Simultaneously with the formation of complex **1** a slow interaction occurs between $YbCl_2(THF)_2$ and the newly formed complex **1**.

We found that in the absence of $YbCl_2(THF)_2$ at room temperature in THF the Yb metal does not react with



In the presence of a catalytic amount of $YbCl_2(THF)_2$ (ca. 4.0 mol%) the interaction between the reagents is completed in ca. 10 h leading to formation of complex **1**. It was also found that in this reaction ytterbium dibromide and ytterbium diiodide exhibit a higher catalytic activity. In the presence of $YbBr_2(THF)_2$ (3–5 mol%) the reaction is complete in ca. 6 h and in the presence of $YbI_2(THF)_4$ (3–5 mol%) in ca. 1 h. Complex **1** has been isolated from these reactions in 85–95% yield.

Recently we observed similar catalytic activity of $YbX_2(THF)_n$ (X = Cl, Br, I) in the reactions of Yb with compounds Ph_3EEPh_3 (E = Si, Ge, Sn) [4,5].

Complexes **1** and **2** are unstable in air, and red and dark-red diamagnetic crystals of **1** and **2** are readily soluble in THF and benzene, but not in hexane. They melt with decomposition at 69–71°C (**1**) and 74–76°C (**2**). IR spectra of **1** and **2** are identical and show the absorption bands of $[Ph_3C]^-$ anions (1550, 1325, 1285, 1250, 1160, 1065, 1010, 980, 820, 740, 725, 695, 600, 550, 500, 410 cm^{-1}) and of coordinated THF (1020, 915, 850 cm^{-1}).

X-Ray diffraction studies have shown that crystals of **1** and **2** have an ionic structure composed of isolated ions.

The ideally octahedral $[Yb(THF)_6]^{2+}$ cation in **1** occupies a special position of $m\bar{3}$ symmetry in crystal and involves the Yb atom bonded to six oxygen atoms of the THF molecules lying on the two-fold axes (Fig. 1). The Yb–O(THF) distance in cation $[Yb(THF)_6]^{2+}$ is 2.390(7) Å.

The $[(THF)_4Yb(\mu\text{-}Cl)_2Yb(THF)_4]^{2+}$ cation in **2** is a centrosymmetrical dimer in which two $(THF)_4Yb$ units are bonded by two symmetrical μ-Cl bridges (Fig. 2). The Yb atom has a distorted octahedral environment. The Yb(1)–Cl(1) and Yb(1)–Cl(1a) distances are both 2.715(4) Å. The Cl(1)Yb(1)Cl(1a) angle is 83.7(2)°. The O(2) and O(4) atoms are displaced from the plane of the central $Yb_2(\mu\text{-}Cl)_2$ fragment by 0.03 and −0.03 Å, respectively. The O(2)Yb(1)O(4) angle of 104.5(4)° is significantly increased in comparison with the ideal octahedral value of 90°. The O(1) and O(3) atoms are bent away from the central part of the cation and the O(1)Yb(1)O(3) angle is 159.5(4)°. The Yb(1)–O(2) and Yb(1)–O(4) distances, 2.39(1) and 2.39(2) Å, for THF molecules in *cis*-position at the Yb(1) atom are identi-

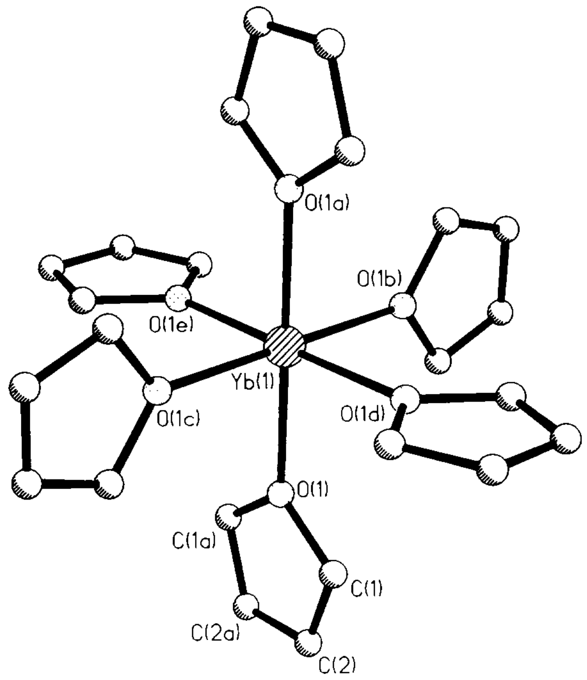


Fig. 1. The general view of the cation $[Yb(THF)_6]^{2+}$ in **1**.

cal and marginally longer than the Yb(1)–O(1) and Yb(1)–O(3) distances, 2.37(1) and 2.36(1) Å, for THF molecules in *trans*-positions.

The structure of the $[(THF)_4Yb(\mu\text{-}Cl)_2Yb(THF)_4]^{2+}$ cation is similar to that of the $[(DME)_3Yb(\mu\text{-}Cl)_2Yb(DME)_3]^{2+}$ cation reported in $[(DME)_3Yb(\mu\text{-}Cl)_2Yb(DME)_3]^{2+}[(Ph_3Sn)_3Sn]_2^-$ [4]. However, the coordination sphere of the Yb atom in the latter compound is formed by two Cl atoms and six O atoms of the DME ligands, whereas in the THF derivative reported in the present paper each Yb atom is coordinated by two Cl and four O atoms. The Yb–Cl (2.769 and 2.772 Å) as well as the Yb–O(DME) (2.48–2.70 Å) distances in the $[(DME)_3Yb(\mu\text{-}Cl)_2Yb(DME)_3]^{2+}$ cation are longer than those in the $[(THF)_4Yb(\mu\text{-}Cl)_2Yb(THF)_4]^{2+}$ cation (2.715, 2.715 Å and 2.36–2.39 Å for Yb–Cl and Yb–O(THF), respectively). These differences may be attributed to a more significant steric overcrowding of the Yb atom in the first case. In both these cations the Yb–Cl distances are longer than those in neutral complexes of lanthanoids, e.g. 2.64 Å in $[(C_5H_4Me)_2Yb(\mu\text{-}Cl)]_2$ [12], 2.65 Å in $[\{C_5H_3(SiMe_3)_2\}_2Yb(\mu\text{-}Cl)]_2$ [13]. The Yb–O(THF) bond lengths of 2.36–2.39 Å observed in $[(THF)_4Yb(\mu\text{-}Cl)_2Yb(THF)_4]^{2+}$ are quite normal for organic Yb derivatives containing THF molecules.

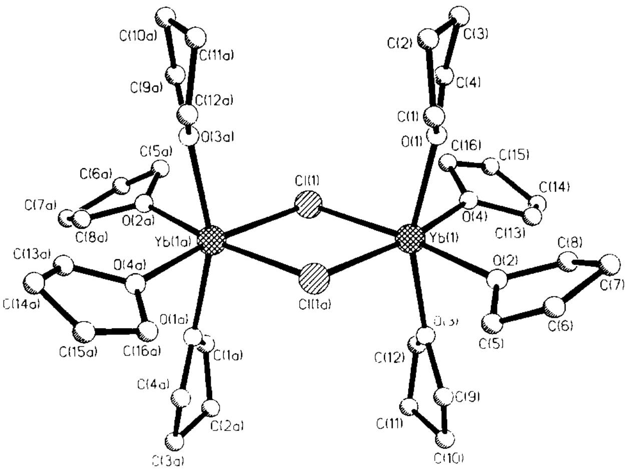


Fig. 2. The general view of the cation $[(THF)_4Yb(\mu\text{-}Cl)]_2^{2+}$ in **2**.

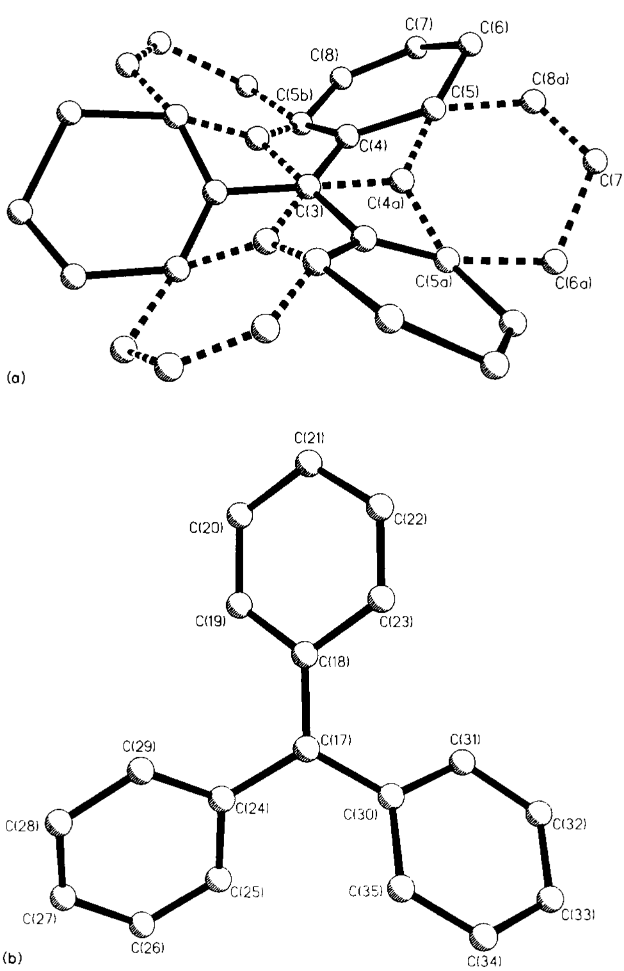


Fig. 3. The structure of the anion $[Ph_3C]^-$ in **1** (a) (one of the disordered $[Ph_3C]^-$ fragments is shown in dashed solid line) and in **2** (b).

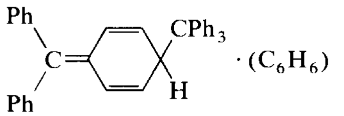
The $[Ph_3C]^-$ anion has a propeller-type structure in **1** as well as in **2** (Fig. 3). In the crystal of **1** there are two disordered positions for the $[Ph_3C]^-$ anion rotated by 60° relative to each other (see Experimental part).

One of these positions is denoted by the dashed line in Fig. 3a. In both structures the central carbon atom of the $[Ph_3C]^-$ anion has a planar environment (within 0.02 Å in **1** and 0.006 Å in **2**). The Ph-rings are planar (within 0.01 Å in **1** and 0.04 Å in **2**) and rotated out of the coordination plane of the central atom of the anion (C(3) in **1** and C(17) in **2**), the angles of rotation being 28.2° in **1** and 26.6, 31.9, 33.7° in **2**. These are slightly smaller than an equilibrium rotation angle of 35 ± 2° for the phenyl rings in the $[Ph_3C]^-$ anion calculated by the extended Hückel method [14]. The C–C distances at the central carbon atom of the $[Ph_3C]^-$ anion are 1.50(2) Å in **1** and C(17)–C(18) 1.42(3) Å, C(17)–C(24) 1.48(2) Å, C(17)–C(30) 1.45(3) Å in **2**. The CCC angles at the central carbon atom of $[CPh_3]^-$ anion are equal to 120° in **1** and close to this value in **2**: C(18)C(17)C(24) 120(2)°, C(18)C(17)C(30) 121(2)°, C(24)C(17)C(30) 119(2)°. Thus, the geometrical parameters of $[Ph_3C]^-$ anions in **1** and **2** are close to those found in $[Li(12\text{-crown-}4)_2][CPh_3](THF)$ [15] containing the isolated $[Ph_3C]^-$ anion and in $Ph_3CM(TMEDA)$ (M = Li [16], Na [17]; TMEDA = N,N,N′,N′-tetramethylethylenediamine) with a contact ion pair of $[Ph_3C]^-$ anion and a lithium (sodium) cation coordinated to the bidentate TMEDA ligand.

3. Experimental part

All operations were performed in vacuo in sealed ampoules. Solvents were thoroughly dried and distilled from sodium/benzophenone solution. The IR spectra were recorded on a Perkin-Elmer 577 spectrometer. Samples of the solids were prepared as suspensions in vaseline oil under dry argon.

Ytterbium dihalides used as catalysts were prepared as follows: $YbCl_2(THF)_2$ by reaction of $YbCl_3$ with Yb in THF; $YbBr_2(THF)_2$ by reaction of Yb with dibromomethane in THF; $YbI_2(THF)_4$ by reaction of Yb with I_2 in THF.



The above complex, used in the reactions with Yb in the presence of ytterbium dihalides, was prepared by reaction of Yb with Ph_3CCl in benzene.

X-Ray diffraction experiments were carried out with a Siemens P3/PC diffractometer at 193 K (λ Mo Kα, θ-2θ scan mode, $2 < 2\theta < 56°$ for **1** and $2 < 2\theta < 50°$ for **2**, 4631 (**1**) and 3418 (**2**) measured reflections, 481 (**1**) and 1818 (**2**) symmetrically independent reflections with $F > 4\sigma(F)$ were used in the refinement).

Crystal data for **1**: $C_{62}H_{78}O_6Yb_1$, cubic, space group $Im\bar{3}$, $a = 14.175(2)$ Å, $V = 2848.2(5)$ Å^3, $Z = 2$, $D_{calc} = 1.27$ g.cm^{-3}, μ (Mo Kα) = 1.69 mm^{-1}.

Crystal data for **2**: $C_{70}H_{94}O_8Cl_2Yb_2$, monoclinic, space group $P2_1/n$, $a = 11.418(2)$, $b = 27.291(3)$, $c = 11.738(4)$ Å, $\beta = 114.78(2)°$, $V = 3321(3)$ Å^3, $Z = 2$, $D_{calc} = 1.48$ g.cm^{-3}, μ (Mo Kα) = 2.93 mm^{-1}.

The structures of **1** and **2** were solved using a combination of direct methods and Patterson function. The $[Ph_3C]^-$ anion in the crystal structure of **1** is disordered over two positions rotated by 60° relative to each other and occupies a special position (1/4, 1/4, 1/4; 3/4, 3/4, 1/4; 3/4, 1/4, 3/4; 1/4, 3/4, 3/4) with the $\bar{3}$ point symmetry (Fig. 3a). The most peculiar feature of the observed type of disorder is associated with the special positions on two different mirror planes occupied by the disordered C(6) atom on the one hand and by the C(7), C(8) atoms, on the other hand. Such a disposition results in formation of the infinite three-dimensional partially occupied anionic framework. The cavities of this framework are filled by the $[Yb(THF)_6]^{2+}$ cations, the Yb atoms occupy the special positions (0, 0, 0) with the $m\bar{3}$ point symmetry. However, the multiplicities of the mentioned special position (2 for $m\bar{3}$ and 8 for $\bar{3}$) are not in accordance with the usual valency of ytterbium (+2 or +3). In order to meet the valency requinements the positions of disordered CPh_3^- groups were treated in the final refinement as partially occupied. Two possible models, which corresponded to two-valent and three-valent ytterbium ($Yb(THF)_6/CPh_3 = 1/2$ and $Yb(THF)_6/CPh_3 = 1/3$, respectively) were tentatively refined. The values of *R*-factors and standard deviations of bond lengths and angles in the first model were slightly better; that is in accordance with the results of elemental analysis for **1** and the fact that crystals of **1** are diamagnetic.

The structure of **1** and **2** were refined with isotropic and anisotropic temperature factors respectively for all non-hydrogen atoms. The H atoms in both structures (except those of the disordered CPh_3 group in **1**) were placed geometrically and refined with fixed isotropic temperature factors ($B_{iso} = 8$ Å^2). In both cases the absorption was taken into account using the DIFABS program [18]. All calculations were performed using

Table 1
Bond lengths (Å) in **1**

Yb(1)–O(1)	2.390(7)	C(4)–C(5)b	1.43(2)
O(1)–C(1)	1.437(9)	C(5)–C(6)	1.72(2)
C(1)–C(2)	1.43(1)	C(6)–C(7)	1.80(3)
C(2)–C(2)a	1.40(2)	C(7)–C(8)	1.45(4)
C(3)–C(4)	1.50(2)	C(8)–C(5)b	1.62(2)
C(4)–C(5)	1.52(2)		

Table 2
Bond angles (deg.) in **1**

Yb(1)–O(1)–C(1)	126.4(4)	C(5)–C(4)–C(5b)	131.2(15)
C(1)–O(1)–C(1a)	107.2(8)	C(4)–C(5)–C(6)	113.7(13)
O(1)–C(1)–C(2)	107.8(7)	C(5)–C(6)–C(7)	114.1(13)
C(1)–C(2)–C(2a)	108.6(5)	C(6)–C(7)–C(8)	115.8(12)
C(3)–C(4)–C(5)	111.7(13)	C(7)–C(8)–C(5b)	125.5(10)
C(3)–C(4)–C(5b)	117.0(14)		

SHELXTL PLUS programs [19]. The final discrepancy factors are: $R = 0.058$ (**1**) and 0.052 (**2**); $R_w = 0.053$ (**1**) and 0.044 (**2**); GOF = 4.81 (**1**) and 1.05 (**2**). The weighting scheme $W^{-1} = \sigma^2(F) + aF^2$ was used ($a = 0.0$ (**1**) and 0.0008 (**2**)). Interatomic distances, bond angles and atomic coordinates with their temperature factors in **1** and **2** are given in Tables 1–6.

3.1. Reaction of Ph_3CCl with Yb in THF

(a) Yb filings (2.86 g, 16.53 mmol) were added to Ph_3CCl (1.50 g, 5.38 mmol) in 25 ml of THF. The mixture was stirred with a magnetic stirrer for 1 h. The reaction mixture was cooled to −40°C and THF was evaporated in vacuo at this temperature. Benzene (20 ml) was added to the dry products and the excess of Yb. Soluble products and a fine white precipitate in the form of a suspension were separated from the excess of Yb. It was found that 0.49 g (2.83 mmol) of Yb was consumed in the reaction. The white precipitate was separated from the solution by centrifugation, washed with benzene (15 ml × 3) and dried in vacuo at room temperature to give 0.55 g (52.9%) of $YbCl_2(THF)_2$. Anal. Found: Cl, 21.40; Yb, 44.33, $C_8H_{16}Cl_2O_2Yb$. Calc.: Cl, 18.28; Yb, 44.58%. The IR spectrum shows the absorption bands of coordinated THF (1040, 910, 875 cm^{-1}).

Dry air was bubbled through the benzene solution for 30 min. The resulting white precipitate was separated by centrifugation, washed with hexane (20 ml × 2) and dried in vacuo to yield 1.18 g (84.3%) of $Ph_3COOCPh_3$, m.p. 183–185°C (mixed m.p.). Anal. Found: C, 88.04; H, 6.44. $C_{38}H_{30}O_2$. Calc.: C, 88.00; H, 5.83%.

Table 3
Atomic coordinates ($\times 10^4$) and isotropic temperature factors U ($Å^2$, $\times 10^2$) in **1**

Atom	*x*	*y*	*z*	*U*
Yb(1)	0	0	0	21(1)
O(1)	1686(5)	0	0	27(2)
C(1)	2288(6)	0	816(6)	42(2)
C(2)	3246(7)	0	494(7)	59(3)
C(3)	2500	2500	2500	19(5)
C(4)	3296(13)	2426(14)	1807(13)	18(4)
C(5)	3049(10)	2883(10)	867(10)	46(3)
C(6)	3871(17)	2689(19)	0	69(7)
C(7)	5000	2295(32)	435(26)	125(14)
C(8)	5000	1902(13)	1380(14)	49(5)

Table 4
Bond lengths (Å) in **2**

Yb(1)–Cl(1)	2.715(4)	C(2)–C(3)	1.50(4)	C(19)–C(20)	1.39(3)
Yb(1)–O(1)	2.37(1)	C(3)–C(4)	1.47(3)	C(20)–C(21)	1.39(2)
Yb(1)–O(2)	2.39(1)	C(5)–C(6)	1.39(3)	C(21)–C(22)	1.39(3)
Yb(1)–O(3)	2.36(1)	C(6)–C(7)	1.54(3)	C(22)–C(23)	1.33(3)
Yb(1)–O(4)	2.39(2)	C(7)–C(8)	1.51(3)	C(24)–C(25)	1.42(3)
Yb(1)–Yb(1a)	4.044(2)	C(9)–C(10)	1.39(4)	C(24)–C(29)	1.39(3)
Yb(1)–Cl(1a)	2.715(6)	C(10)–C(11)	1.53(3)	C(25)–C(26)	1.38(2)
O(1)–C(1)	1.46(3)	C(11)–C(12)	1.43(3)	C(26)–C(27)	1.38(3)
O(1)–C(4)	1.44(3)	C(13)–C(14)	1.52(4)	C(27)–C(28)	1.34(3)
O(2)–C(5)	1.47(3)	C(14)–C(15)	1.40(3)	C(28)–C(29)	1.44(3)
O(2)–C(8)	1.39(2)	C(15)–C(16)	1.39(4)	C(30)–C(31)	1.43(3)
O(3)–C(9)	1.43(2)	C(17)–C(18)	1.42(3)	C(30)–C(35)	1.45(3)
O(3)–C(12)	1.50(4)	C(17)–C(24)	1.48(2)	C(31)–C(32)	1.42(3)
O(4)–C(13)	1.42(2)	C(17)–C(30)	1.45(3)	C(32)–C(33)	1.37(3)
O(4)–C(16)	1.47(2)	C(18)–C(19)	1.39(3)	C(33)–C(34)	1.35(3)
C(1)–C(2)	1.45(3)	C(18)–C(23)	1.44(2)	C(34)–C(35)	1.42(3)

Table 5
Bond angles (deg.) in **2**

Cl(1)–Yb(1)–O(1)	99.2(3)	O(3)–C(9)–C(10)	112.4(22)
Cl(1)–Yb(1)–O(2)	170.7(3)	C(9)–C(10)–C(11)	104.8(16)
O(1)–Yb(1)–O(2)	82.6(4)	C(10)–C(11)–C(12)	102.9(20)
Cl(1)–Yb(1)–O(3)	96.7(3)	O(3)–C(12)–C(11)	108.1(20)
O(1)–Yb(1)–O(3)	159.5(4)	O(4)–C(13)–C(14)	104.7(16)
O(2)–Yb(1)–O(3)	83.8(4)	C(13)–C(14)–C(15)	105.7(21)
Cl(1)–Yb(1)–O(4)	84.8(3)	C(14)–C(15)–C(16)	110.8(22)
O(1)–Yb(1)–O(4)	84.9(5)	O(4)–C(16)–C(15)	107.5(16)
O(2)–Yb(1)–O(4)	104.5(4)	C(18)–C(17)–C(24)	119.6(18)
O(3)–Yb(1)–O(4)	83.8(5)	C(18)–C(17)–C(30)	121.2(16)
Cl(1)–Yb(1)–Cl(1a)	83.7(2)	C(24)–C(17)–C(30)	119.3(17)
O(1)–Yb(1)–Cl(1a)	96.3(4)	C(17)–C(18)–C(19)	125.2(14)
O(2)–Yb(1)–Cl(1a)	87.0(3)	C(17)–C(18)–C(23)	122.6(17)
O(3)–Yb(1)–Cl(1a)	98.2(4)	C(19)–C(18)–C(23)	112.0(16)
O(4)–Yb(1)–Cl(1a)	168.5(3)	C(18)–C(19)–C(20)	125.8(15)
Yb(1)–Cl(1)–Yb(1a)	96.3(2)	C(19)–C(20)–C(21)	118.7(18)
Yb(1)–O(1)–C(1)	124.3(11)	C(20)–C(21)–C(22)	117.6(19)
Yb(1)–O(1)–C(4)	124.7(15)	C(21)–C(22)–C(23)	122.2(16)
C(1)–O(1)–C(4)	109.8(16)	C(18)–C(23)–C(22)	123.2(18)
Yb(1)–O(2)–C(5)	129.7(10)	C(17)–C(24)–C(25)	120.8(20)
Yb(1)–O(2)–C(8)	122.8(11)	C(17)–C(24)–C(29)	121.9(17)
C(5)–O(2)–C(8)	107.3(13)	C(25)–C(24)–C(29)	117.2(15)
Yb(1)–O(3)–C(9)	129.7(16)	C(24)–C(25)–C(26)	121.8(21)
Yb(1)–O(3)–C(12)	126.7(10)	C(25)–C(26)–C(27)	119.7(18)
C(9)–O(3)–C(12)	103.5(17)	C(26)–C(27)–C(28)	120.6(18)
Yb(1)–O(4)–C(13)	122.7(11)	C(27)–C(28)–C(29)	120.8(22)
Yb(1)–O(4)–C(16)	129.8(12)	C(24)–C(29)–C(28)	119.7(18)
C(13)–O(4)–C(16)	107.5(16)	C(17)–C(30)–C(31)	122.2(17)
O(1)–C(1)–C(2)	103.4(19)	C(17)–C(30)–C(35)	120.3(17)
C(1)–C(2)–C(3)	108.4(21)	C(31)–C(30)–C(35)	117.5(18)
C(2)–C(3)–C(4)	101.5(17)	C(30)–C(31)–C(32)	118.6(17)
O(1)–C(4)–C(3)	107.4(20)	C(31)–C(32)–C(33)	123.2(20)
O(2)–C(5)–C(6)	107.1(16)	C(32)–C(33)–C(34)	118.6(22)
C(5)–C(6)–C(7)	109.1(21)	C(33)–C(34)–C(35)	122.9(18)
C(6)–C(7)–C(8)	101.5(15)	C(30)–C(35)–C(34)	119.1(17)
O(2)–C(8)–C(7)	108.8(18)		

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors U (Å^2, $\times 10^3$) in **2**

Atom	x	y	z	U
Yb(1)	1039(1)	5617(1)	5684(1)	35(1)
Cl(1)	274(5)	5052(2)	3592(4)	50(2)
O(1)	−618(14)	6212(5)	4960(12)	68(8)
O(2)	1556(12)	6015(4)	7653(10)	47(6)
O(3)	3122(12)	5276(5)	6724(11)	52(6)
O(4)	2041(13)	6111(5)	4668(10)	58(7)
C(1)	−1571(21)	6281(8)	5472(19)	78(12)
C(2)	−2621(23)	6533(8)	4469(19)	84(13)
C(3)	−2078(21)	6802(7)	3689(17)	63(11)
C(4)	−999(22)	6483(8)	3802(18)	83(13)
C(5)	1378(19)	5845(7)	8759(16)	56(10)
C(6)	1182(22)	6259(7)	9350(17)	78(13)
C(7)	1608(22)	6716(6)	8854(16)	63(12)
C(8)	2011(19)	6493(6)	7891(15)	52(10)
C(9)	3832(26)	5155(12)	8021(18)	129(18)
C(10)	5026(22)	4944(7)	8264(19)	70(13)
C(11)	4930(22)	4785(8)	6977(19)	84(13)
C(12)	3999(25)	5120(9)	6137(20)	88(15)
C(13)	3046(20)	6450(8)	5329(17)	61(11)
C(14)	3719(25)	6534(10)	4474(20)	115(16)
C(15)	2841(20)	6387(9)	3281(19)	84(13)
C(16)	1839(24)	6120(8)	3349(15)	90(14)
C(17)	6189(18)	6697(7)	8914(15)	41(9)
C(18)	6934(17)	6277(6)	8937(15)	29(9)
C(19)	6964(20)	6051(7)	7883(16)	50(10)
C(20)	7617(20)	5622(8)	7884(16)	60(11)
C(21)	8357(20)	5399(7)	9024(17)	60(11)
C(22)	8375(18)	5616(8)	10107(15)	53(9)
C(23)	7653(18)	6005(8)	10067(16)	46(10)
C(24)	5860(19)	7056(6)	7878(14)	36(9)
C(25)	4695(20)	7331(6)	7458(14)	45(10)
C(26)	4356(18)	7659(6)	6478(15)	38(9)
C(27)	5183(19)	7740(7)	5911(17)	46(10)
C(28)	6321(19)	7506(7)	6315(16)	51(10)
C(29)	6696(19)	7160(6)	7331(15)	45(9)
C(30)	5728(16)	6777(7)	9878(16)	43(9)
C(31)	5353(16)	6382(7)	10455(15)	40(9)
C(32)	4846(19)	6493(7)	11339(16)	51(10)
C(33)	4674(21)	6964(8)	11656(16)	63(11)
C(34)	5057(17)	7340(7)	11142(15)	42(9)
C(35)	5591(16)	7271(7)	10261(13)	35(8)

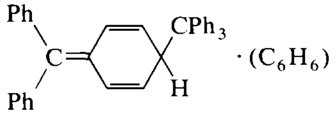
(b) Yb filings (3.12 g, 18.03 mmol) were added to Ph_3CCl (1.50 g, 5.38 mmol) in 25 ml of THF. The mixture was stirred using a magnetic stirrer at room temperature. The solution became pale-yellow and white precipitate was formed. Then (after ca. 1 h of stirring) the solution became red coloured. Upon the subsequent stirring of the reaction mixture the intensity of this red colour increased and the precipitate partially dissolved. After 3 h from the beginning of the reaction the solution and the precipitate were separated from the excess of Yb. It was found that 0.91 g (5.26 mmol) of Yb was consumed in the reaction. The precipitate was separated from the reaction solution, washed repeatedly with THF and dried in vacuo at room temperature to yield 0.23 g (22.1%) of $YbCl_2(THF)_2$ (identified by elemental analysis and IR spectrum). The reaction solution was concentrated to approx. 15 ml, cooled and kept at 0°C for 24 h to yield a mixture of crystals of two types: red tetragonal bipyramids of **1** and dark-red parallelepipeds of **2**. Both types of crystals were isolated and identified by X-ray study.

(c) Yb filings (2.57 g, 14.85 mmol) were added to Ph_3CCl (1.50 g, 5.38 mmol) in 25 ml of THF. The mixture was stirred using a magnetic stirrer for 15 h at room temperature. The dark-red reaction solution and dark-red precipitate were separated from the excess of Yb. It was found that 0.88 g (5.09 mmol) of Yb was consumed in the reaction.

The solution was separated from the precipitate. The dark-red precipitate was then completely dissolved by repeated extraction with THF. Ytterbium dichloride, (insoluble in THF), was not found in the reaction mixture. Dark-red solution and all extracts were combined and THF was evaporated in vacuo to yield a dark-red solid of crude complex **2** (3.49 g, 87.7%). Anal. Found: C, 56.40; H, 5.92; Cl, 3.98; Yb, 22.33. $C_{70}H_{94}Cl_2O_8Yb_2$. Calc.: C, 56.79; H, 6.40; Cl, 4.79; Yb, 23.38%. Crude complex **2** was dissolved in THF (25 ml) at 50°C and the solution was slowly cooled to room temperature to yield dark-red crystals (1.50 g, 37.7%) of complex **2**. Anal. Found: C, 57.09; H, 6.55; Cl, 5.07; Yb, 23.57%. IR: 1545, 1325, 1280, 1250, 1160, 1065, 1020, 980, 915, 855, 815, 745, 725, 695, 600, 550, 500, 410 cm^{-1}. M.p. 74–76°C (dec.).

3.2. *Reaction of Ph_3CCl with Yb in benzene*

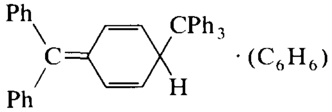
Yb filings (2.42 g, 13.99 mmol) were added to Ph_3CCl (1.50 g, 5.38 mmol) in 25 ml of benzene. The mixture was stirred with a magnetic stirrer at room temperature. The reaction was monitored periodically by checking the chlorine content in the reaction solution; after ca. 200 h chlorine was not found there. The light-yellow solution and fine grey precipitate were separated from the excess of Yb. It was found that 0.45 g (2.60 mmol) of Yb was consumed in the reaction. The precipitate was separated by centrifugation, washed repeatedly with benzene and dried in vacuo at room temperature to yield 0.46 g (69.7%) of $YbCl_2$. Benzene was removed from the solution and the residue was dried in vacuo at room temperature to yield a light-yellow solid (1.44 g, 94.7%) of crude dimer of triphenylmethyl) radicals. Found: C, 93.14; H, 6.39. $C_{44}H_{36}$. Calc.: C, 93.99, H, 6.43%. After crystallization from benzene/hexane (2/1) at 5°C for 20 h light-yellow crystals (0.89 g, 58.6%) of



were obtained. M.p. 140–144°C (dec.) IR: 1470, 1250, 1055, 1025, 930, 915, 900, 805, 770, 745, 735, 715, 690, 665, 635, 625, 610, 515 cm^{-1}. Anal. Found: C, 93.23; H, 6.47. $C_{44}H_{36}$. Calc.: C, 93.99, H, 6.43%.

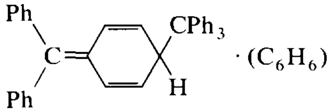
3.3. *Reaction of the complex shown with Yb in the presence of YbCl$_2$(THF)$_2$*

Yb filings (2.86 g, 16.53 mmol) were added to a mixture of



(0.67 g, 1.19 mmol) and $YbCl_2(THF)_2$ (0.02 g, 0.05 mmol) in 25 ml of THF. The mixture was stirred using a magnetic stirrer at room temperature for 10 h. The red solution and light-red precipitate were separated from the excess of Yb. It was found that 0.20 g (1.16 mmol) of Yb was consumed in the reaction. THF was evaporated from the solution with the precipitate to give 1.34 g (103.1%) of crude complex **1**. Anal. Found: C, 65.99; H, 6.70; Yb, 18.30. $C_{62}H_{78}O_6Yb$. Calc.: C, 68.17; H, 7.19; Yb, 15.84%. The crude complex **1** was dissolved in 20 ml of THF at 50°C and the solution was cooled slowly to room temperature to yield red crystals (1.07 g, 82.3%) of complex **1**. Anal. Found: C, 68.00; H, 7.24; Yb, 15.48%. IR 1550, 1325, 1285, 1250, 1160, 1060, 1010, 980, 915, 850, 820, 740, 725, 695, 600, 550, 500, 410 cm^{-1}. M.p. 69–71°C (dec.).

Reactions of



with Yb in the presence of $YbBr_2(THF)_2$ and $YbI_2(THF)_4$ were carried out in a similar manner. It was found that in the presence of ytterbium dibromide (4.0% mol) the reaction is completed in ca. 6 h. The yield of **1** in this case is 88.5%. In the presence of ytterbium diiodide (3.5% mol) the reaction is completed in ca. 1 h. The complex **1** in this case was isolated in 94.5% yield.

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