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Synthesis and structural studies of heteroleptic complexes of ytterbium(III) involving aryloxy- or alkoxy- and cyclopentadienyl ligands [☆]

Thilo Hahn^a, Evamarie Hey-Hawkins^{a,*}, Matthias Hilder^b, Peter C. Junk^{b,*}, Matthew K. Smith^{b,1}

> ^a Institut für Anorganische Chemie der Universität Leipzig, D-04103 Leipzig, Germany ^b School of Chemistry, Monash University, P.O. Box 23, Clayton, Vic. 3800, Australia

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Abstract

Treatment of tris-cyclopentadienyl-ytterbium in thf with one equivalent of 2,6-di(*tert*-butyl)phenol, *N*,*N*-dimethyl-2-aminoethanol resulted in substitution of one cyclopentadienyl ligand and formation of [YbCp₂(O-C₆H₃'Bu-2,6)(thf)] (1), [{YbCp₂(μ -OCH₂CH₂NMe₂)}₂] (2) or [{YbCp₂(μ -OCH₂CH₂NEt₂)}₂] (thf)₂ (3), respectively. All compounds were characterised by spectroscopic and X-ray crystallographic techniques, the latter two also being studied by variable temperature ¹H NMR spectroscopy. Compound (1) is mononuclear with the Yb centre bound by two η⁵-cyclopentadienyl ligands, one O-bound thf and an O-bound phenoxy ligand. Compounds (2) and (3) are centrosymmetric dimers with the Yb centre bound by two η⁵-cyclopentadienyl ligands, while the bidentate ligands chelate the metal centre and also bridge to the adjacent Yb through the alkoxy oxygen atom. Variable temperature ¹H NMR studies on compounds (2) and (3) show a solution-state equilibrium between the dimeric solid-state structure and one with the nitrogen atoms non-bound to Yb. © 2003 Elsevier B.V. All rights reserved.

Keywords: Ytterbium; Aryloxides; Cyclopentadienyl; Alkoxides; X-ray structures

1. Introduction

The cyclopentadienyl ligand is ubiquitous in organolanthanoid chemistry [1]. Tris-cyclopentadienyl lanthanoid complexes have found uses in chemical vapour deposition of rare earths into group 13–15 (III–V) semiconductors [2] but also as useful starting materials for the synthesis of heteroleptic lanthanoid complexes [3–12]. Treatment of LnCp₃ complexes with compounds of greater thermodynamic acidity than CpH, can result in substitution of the Cp ligand, and therefore, by judicious choice of ligand and stoichiometry, the synthesis of heteroleptic complexes can be achieved. Heteroleptic lanthanoid compounds have extensive applications as catalysts in a wide range of reactions [13-22]. In homogenous catalysis, the co-ligand can have a large influence on the catalytic activity and selectivity, and the catalytic properties of these complexes can be fine-tuned by modifying the co-ligands [23]. Additionally, the heteroleptic complexes can be more stable towards hydrolysis. Some of them can even be used in protic organic reaction media or even in water. Co-ligands that have an intramolecular heteroatom (O, N, P) that can form a coordinative bond through chelation are attractive in the quest for heteroleptic lanthanoid catalysts. These heteroatoms can form intramolecularly solvated complexes which can be involved in equilibria with their unsolvated counterparts in solution [24-27]. Thus, formally coordinatively unsaturated metal centres that

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^{*} Corresponding authors. Tel.: +61399054570; fax: +61399054597.

E-mail addresses: hey@rz.uni-leipzig.de (E. Hey-Hawkins), peter.junk@sci.monash.edu.au (P.C. Junk).

¹ Visiting student from the Department of Chemistry, James Cook University, Townsville, Qld. 4811, Australia.

can be involved in small molecule catalysis are generated. Such heteroatoms would preferably be atoms that would form only moderate interactions with the metal centre, and for the lanthanoid elements, the softer donor atoms N and P are preferential.

This present paper describes the substitution of one cyclopentadienyl ligand by a phenolato (2,6-di(tert-butyl)phenol) or aminoalcoholato $(N,N\text{-dimethyl-2-aminoethanol}, N,N\text{-diethylaminoethanol}, respectively) co-ligand by treating tris-cyclopentadienyl ytterbium with the respective alcohol. Thus, we report herein, the synthesis and characterisation of <math>[YbCp_2(O-C_6H_3^TBu-2,6)(thf)]$ (1), $[\{YbCp_2(\mu\text{-OCH}_2CH_2NMe_2)\}_2]$ (2) and $[\{YbCp_2(\mu\text{-OCH}_2CH_2NEt_2)\}_2] \cdot (thf)_2$ (3).

2. Results and discussion

Compounds (1) to (3) were conveniently synthesised by treating [YbCp₃(thf)] with an equimolar amount of the alcohols 2,6-di(*tert*-butyl)phenol, *N*,*N*-dimethyl-2aminoethanol or *N*,*N*-diethyl-2-aminoethanol, respectively, as shown in Eq. (1) [28,29]. The Brønstedt acidity of the co-ligand dictates whether substitution takes place. To substitute the Cp ligand its acidity must be greater than that of HCp and in this case, the pK_a of each of the alcohols is approx. 9–10 compared with a pK_a of approx. 15 for cyclopentadiene.

$$[YbCp_{3}(thf)] + R-OH \xrightarrow{tht} [YbCp_{2}(O-R)]_{m}(thf)_{n} + HCp$$
(1)

- (1), R = 2,6-di(tert-btuyl) phenyl; m = 1, n = 1,
- (2), R = N, N-dimethylaminoethyl; m = 2, n = 0,
- (3), R = N, N-diethylaminoethyl; m = 2, n = 2.

The first co-ligand investigated was 2,6-di(*tert*-butyl)phenol. Due to resonance stabilisation effects of the phenolate anion it shows a remarkable acidity. Furthermore, since it contains the two bulky substituents in the 2,6-positions, it was envisaged that based on steric effects, the nuclearity could be restricted to a monomeric species. Indeed, by letting [YbCp₃(thf)] react with one molar equivalent of 2,6-di(*tert*-butyl)phenol red single crystals suitable for X-ray diffraction analysis were isolated from thf.

[YbCp₂(O-C₆H₃^{*t*}Bu-2,6)(thf)] (1) crystallises in the monoclinic space group $P2_1/c$ with one monomeric entity constituting the asymmetric unit (Fig. 1). Selected bond lengths and angles are given in Table 1. The eightcoordinate Yb centre is bound by two η^5 -cyclopentadienyl, one phenolato ligand as well as one thf molecule. Evidently, the phenolato ligand is not sufficiently bulky to prevent the coordination of solvent molecules. The four ligands form a distorted tetrahedral (if the centroids of the Cp rings are considered the point of binding to the Yb centre) environment around Yb.



Fig. 1. X-ray crystal structure of mononuclear $[YbCp_2(O-C_6H_3^{T}Bu_2-2,6)(thf)]$ (1). Hydrogen atoms have been removed for clarity.

The Yb–Cp(centroid) distances of 2.345 and 2.353 Å are similar to those in another related eight-coordinate cyclopentadienyl complex involving Yb^{III}, e.g. [YbCp₂(OC₁₀H₇)(thf)] (where the average Yb–Cp(centroid) distance is 2.310 Å) [7]. The Yb–O_(thf) distance is significantly longer (2.385(4) Å) as expected than for the phenolato ligand (2.127(4) Å). The Cp_{centroid}–Yb–Cp_{centroid} angle is 124.9(4)°.

In general the structure is primarily governed by the bulkiness of the phenolato ligand, thus preventing oligoor polymerisation and having a stabilising influence for formation of a monomeric species. The Yb-O-C(arvl) angle $(149.6(4)^{\circ})$ is significantly more obtuse than for an sp³ hybridised oxygen atom, but also departs substantially from linearity. The Cp_(centroid)-Yb-O angles are 99.6° and 104.8° (for thf), whereas they are 108.4° and 115.5° for the phenolato ligand. The deviation from tetrahedral geometry is due to the steric bulk of the phenolato ligand. Interestingly, the solvent-free complexes of the composition [SmCp $_2$ (O-C₆H₂- t Bu₃-2,4,6)] [30] and $[SmCp*_2(O-C_6HMe_4-2,3,5,6)]$ [31] (Cp*=pentamethylcyclopentadienyl) have been previously studied. Even though the phenolato ligands have similar steric bulk about the lanthanoid centre, the Cp* ligands are sterically much more demanding than non-substituted Cp, and thus, a solvent-free species was obtained. In accordance with this is the observation that the neodymium phenolato complex [NdCp₂(O-C₆H₃-Ph₂-2,6)(thf)] is obtained with coordinating thf [32]. In compound (1), the sp² hybridised α -carbon atom of the phenyl ring lies within the ring plane whereas the $C(CH_3)_3$ atoms of the two *tert*-butyl groups reside out of this plane by -0.343(6) and -0.323(7) Å, respectively, while the phenolato oxygen atom lies out of this plane by 0.246(4) A giving the phenolato group a curved conformation away from the metal centre. There is a reasonably close contact between the Yb centre and two

Table 1 Selected bond (i) distances (Å) and (ii) angles (°) for $[YbCp_2(O-C_6H_3^TBu_2-2,6)(thf)]$ (1)

Atoms	Distance	Atoms	Distance
(i)			
Yb(1)–O(1)	2.127(4)	Yb(1)– $Cen(1)$	2.345
Yb(1)–O(2)	2.385(4)	Yb(1)–Cen(2)	2.353
Atoms	Angle	Atoms	Angle
(ii)			
O(1)-Yb(1)-O(2)	99.0(2)	Cen(1)-Yb(1)-Cen(2)	124.9
Cen(1)-Yb(1)-O(1)	108.4	Cen(1)-Yb(1)-O(2)	104.8
Cen(2)-Yb(1)-O(1)	115.5	Cen(2)–Yb(1)–O(2)	99.7

protons of the *tert*-butyl groups with distances of 3.015 and 2.810 Å and may be considered as agostic interactions. Such interactions with similar distances have been reported before for $[Sm(\mu, \eta^5-Cp^*)_2(O-C_6H_2-^tBu_2-2, 6-$ Me-4)(thf)₂K] [30]. Wu and coworkers [7] reported a related compound involving a naphtholato ligand, viz [YbCp₂(OC₁₀H₇)(thf)]. Bond distances, angles and structural parameters are comparable to the present compound. Some angles however reflect the fact that the naphtholato ligand is sterically less demanding than the phenolato ligand. The Cpcentroid-Yb-Cpcentroid angle for example is about 6° smaller for the phenolato ligand than it is for the naphtholato ligand. Other angles involving Yb obey the same trend implying that the phenolato ligand repels the other ligands to a greater extent. These two structures are the only Yb complexes involving Cp as well as aryloxo co-ligands. Besides the above mentioned Sm [30,31] and Nd [32] complexes, a closely related Ti^{III} compound, viz [TiCp₂(O-C₆H₂-2,6-^tBu-4-Me)], was reported by Lappert and coworkers [33], which has, while unsolvated, similar bonding parameters to the present complex. The Ti–O–C(aromatic) angle of $142.3(2)^{\circ}$ is slightly more acute than that in compound (1). The tertiary carbon atoms C (CH₃)₃ of the tert-butyl group also resides out of the plane (0.36 Å) defined by the aromatic ring in a similar manner as described for compound (1).

Our question now was, how would the structure change if another class of co-ligand was introduced to the system? In place of phenolato ligands it was our intention to study alcoholato ligands. The electronic properties of these saturated aliphatic compounds are very different to their aromatic relatives. This results in much less acidic OH groups compared to phenolic OH groups. Additionally, they are sterically less demanding than the phenyl ring with two *tert*-butyl groups adjacent to the alcohol residue. Oligo- or polymerisation or the coordination of solvent molecules could therefore be expected. To prevent these phenomena it was decided to use bifunctional co-ligands (N,N-dimethyl-2-aminoethanol and N,N-diethyl-2-aminoethanol) whose additional electron-donor atoms could bind to the metal centre and coordinatively saturate Yb^{III}.

Following the same route as described above (see Eq. (1)) [YbCp₃(thf)] was treated with one equivalent of the aliphatic aminoalcohol in thf. From the reaction mixtures yellow-orange single crystals could be obtained which were suitable for X-ray diffraction analysis.

The X-ray crystal structures of $[{YbCp_2(\mu - OCH_2CH_2NMe_2)}_2]$ (2) and $[{YbCp_2(\mu - OCH_2CH_2NEt_2)}_2] \cdot (thf)_2$ (3) in the solid state are shown in Figs. 2 and 3 and selected bond lengths and angles are compiled in Table 2.

Compounds (2) and (3) represent the second structural reports of heteroleptic lanthanoid cyclopentadienyl complexes containing aminoalcoholates as ligands. Related lanthanoid complexes (R, R)-[{LnCp₂(μ -OCH₂CH-(Et)NMe₂)}₂] (Ln = Nd, Sm, Tb, Y) [34], were reported recently. Both compounds (1) and (2) have similar dimeric structures which reside on a centre of inversion. The Yb centre is bound by two η^5 -cyclopentadienyl ligands and an aminoalcoholato ligand which chelates via the N and O atoms and also bridges to the other Yb centre (via the oxygen atom) resulting in nine-coordination about Yb. The environment around the ytterbium centre can be described as a distorted trigonal bipyramid (if the



Fig. 2. X-ray crystal structure of dimeric $[{YbCp_2(\mu - OCH_2CH_2NMe_2)}_2]$ (2). Hydrogen atoms have been removed for clarity.



Fig. 3. X-ray crystal structure of dimeric $[{YbCp_2(\mu - OCH_2CH_2NEt_2)}_2] \cdot (thf)_2$ (3). Hydrogen atoms and lattice thf molecules have been removed for clarity.

centroids of the Cp rings are considered the points of attachment to Yb) where the nitrogen and the bridging oxygen atoms occupy the apical positions of the polyhedron. The distances between the two Yb centres are 3.7072(6) Å for [{YbCp₂(μ -OCH₂CH₂NMe₂)}₂] and 3.6910(8) Å for [{YbCp₂(μ -OCH₂CH₂NEt₂)}₂] · (thf)₂, which rule out direct metal-metal interactions.

The Cp_{cen}-Yb-Cp_{cen} angles for $[{YbCp_2(\mu-OCH_2 CH_2NMe_2)}_2]$ and $[{YbCp_2(\mu-OCH_2CH_2NEt_2)}_2]$. (thf)₂ are 121.8 and 123.2°, respectively, being similar to the phenolato co-coordinated compound (1) above. The Yb–O_(chelate) and Yb–O_(bridging) distances for [{YbCp₂(μ -OCH₂CH₂NMe₂)}₂] are 2.224(4) and 2.273(3) Å, whereas they are 2.193(5) and 2.273(5) Å for [{YbCp₂(μ -OCH₂CH₂NEt₂)}₂] · (thf)₂. It is worthy to mention that these Yb–O distances are significantly longer than Yb–O_{phenolato} in compound (1), but this could be expected based on an increase in coordination number. The Yb₂O₂ core is necessarily planar by symmetry. Such subunits have been reported before for ytterbium alcoholato complexes [6,35–41] as well as with phenolato ligands [42].

The most distinguishable feature between the two structures is the bond length difference of the Yb–N bond. In compound (2) this distance is 2.691(4) Å, whereas it is significantly longer (2.895(7) Å) in compound (3). The reason for this bond lengthening in compound (3) is mysterious and the only explanation is that the ethyl group is more sterically demanding than the methyl groups in (2). The distances are still longer than those involving other tertiary amines in ytterbium(III) complexes (e.g. [YbNa(L)Cl₂]·MeOH (with $L = N_3, O_5$ macrocyle)) where the Yb–N distance is 2.593(4) Å [43].

In the case of the aminoalcoholato complexes there is no doubt that in the solid state Yb is coordinated by oxygen as well as by nitrogen. It was also of interest to understand the nature of compounds (2) and (3) in solution. Of special interest is the coordinative nature of the Yb–N bond. If the Yb–N bond is cleaved in solution the metal can become coordinatively unsaturated, opening the possibility of catalytic activity. Some possible conformations of these dinuclear species in solution in equilibrium are shown in Fig. 4.

Table 2

Selected bond parameters for $[\{YbCp_2(\mu-OCH_2CH_2NMe_2)\}_2]$ (2) and $[\{YbCp_2(\mu-OCH_2CH_2NEt_2)\}_2] \cdot (thf)_2$ (3)

	Compound (1) Distances in Å, angles in °		Compound (2)	
			Distances in Å, angles in °	
Yb(1)–O(1)	2.224(4)		2.193(5)	
Yb(1)–O(1')	2.273(3)		2.273(5)	
Yb(1)Yb(1')	3.7072(6)		3.6910(8)	
Cen(1)-Yb(1)	2.414		2.392	
Cen(2)-Yb(2)	2.406		2.397	
O(1)-Yb(1)-O(1')		69.0(2)		68.6(2)
Yb(1)–O(1)–Yb(1')		111.1(2)		111.4(2)
Cen(1)-Yb(1)-Cen(2)		121.8		123.2



Fig. 4. Stepwise mechanism of ring opening with some possible conformations.

This ring opening mechanism would provide two major advantages. Firstly, after the ring opening, the coordination sphere around the Yb cation would be less saturated due to the lack of coordination by the nitrogen. These coordinatively unsaturated centres avail coordination sites for substrate binding, thus resulting in a higher potential catalytic activity. Secondly, the ring opening will lead to a free electron pair on the nitrogen atom to which another metallic complex could be bound. Heterobimetallic catalysts with two different catalytic active centres could therefore be obtained [44]. In other words if we could demonstrate opening of the chelate ring in solution, the potential for catalytic activity could be increased dramatically.

 Yb^{3+} is strongly paramagnetic. The presence of paramagnetic compounds changes the chemical shift of organic fragments significantly. In the presence of Yb^{3+} complexes the scale of an ¹H NMR spectrum can therefore expand up to 290 ppm. It was decided to determine if ring opening occurs by NMR spectroscopy. The solvent of choice was dried, deuterated chloroform, which is sufficiently polar to dissolve appreciable quantities of the lanthanoid complexes for NMR studies, without coordinating to the metal centre.

It is possible that an equilibrium between dimeric and monomeric species exists:

$$[\{YbCp_2(OCH_2CH_2NR_2)\}_2]$$

$$\Leftrightarrow 2 [YbCp_2(OCH_2CH_2NR_2)]$$
(2)

Fischer and coworkers [34,40] have performed NMR experiments (VT NMR experiments in solution and, for some complexes, NMR studies in the solid state) on comparable bis-cyclopentadienyl complexes (R, R)-[{LnCp₂(μ -OCH₂CH(Et)NMe₂)}₂] (Ln = La, Pr, Nd, Sm, Tb, Y, Tm, Yb, Lu). A mixture of two different homodinuclear complexes did not show signals of heterodinuclear complexes in the ¹H NMR spectrum

(metathetical exchange) [34]. From this result it can be assumed that even in solution the dimeric core is maintained. This will presumably be also the case in the present complexes (2) and (3).

¹H NMR spectra of [{YbCp₂(μ -OCH₂CH₂NMe₂)}₂] were recorded in the range of -100 to 300 ppm at various temperatures. Fig. 5 shows the change of the chemical shift with temperature, whereas Fig. 6 shows the dependence of the signal width with the temperature.

The spectrum at room temperature shows four signals in the range of -23.3 to 75.7 ppm. At room temperature the Cp ligand shows a signal at -23.3 ppm (20 H). The methyl group protons are at 64.6 ppm in resonance (12 H). There are two signals at 58.7 ppm (4 H) and 75.7 ppm (4 H) which belong to either the N-CH₂ or the O-CH₂ protons. Since the intensities are the same a proper assignment of the peaks is difficult. The signal at 75.7 ppm is attributed to the $O-CH_2$ group due to the greater electronegativity of O compared with N, whereas the signal at 58.7 ppm is assigned to the N-CH₂ group. None of the signals show any fine structure, which leads to the assumption that the complex exists in its open structure (N non-bound to Yb) at room temperature. At lower temperatures, the Cp signals are shifted to lower frequencies (upfield), whereas the other signals are shifted towards higher frequencies (downfield). A plot of the temperature dependence of the chemical shift shows a nearly linear relationship between δ and T, indicating a continuous change of the magnetic moments probably due to slight structural changes (Fig. 5). These changes of the chemical shift with varying temperature are hard to analyse. The main reason is an anisotropic effect of the magnetic moment of the paramagnetic Yb^{3+} , which is hard to predict.

As expected the line width increases with decreasing temperature (Fig. 6). The line width for the Cp ligands for example is 110 Hz at 25 °C, whereas it is 4000 Hz at



Fig. 5. Temperature dependence of the chemical shifts in the ¹H NMR spectrum of $[{YbCp_2(\mu-OCH_2CH_2NMe_2)}_2]$ (2).



Fig. 6. Temperature dependence of the ¹H NMR signal widths in [$\{YbCp_2(\mu-OCH_2CH_2NMe_2)\}_2$] (2).

-38 °C. At high temperatures it seems that the complex exists in its open structure. The Cp ligands can rotate freely and therefore all protons on the ligand are equivalent which results in one sharp signal. At lower temperatures the interaction between Yb and N increases which leads to a limited mobility of the Cp ligands. The protons of the two Cp ligands become non-equivalent and line widening occurs. This line broadening can also be observed for the two sets of methylene protons. The line broadening for the methyl protons is less significant. It appears that the N–C_{methyl} bond is insignificantly affected by the increased interaction between Yb and N.

From these results it can be assumed that at high temperatures the open structure is formed. With decreasing temperature the interaction between Yb and N increases. The broad lines however indicate that there are different structural species in equilibrium.

VT-¹H NMR studies of the compounds [{YbCp₂(μ -OCH₂CH₂NEt₂)}₂]·(thf)₂ as well as of the solvent free

analogue [{YbCp₂(μ -OCH₂CH₂NEt₂)}₂] were recorded. The results are shown in Figs. 7 and 8.

In the temperature range of 30 to -40 °C the spectra do not differ significantly. The presence of thf in the lattice does not initiate any significant structural changes. The coordinated Cp protons are at a chemical shift of -56.2 ppm (20 H). The CH₂ protons of the N– CH₂CH₃ group show a signal at 77.0 ppm (8 H) and the signal for the CH₃ protons of the same group occurs at 48.5 ppm (12 H). There are two signals for the methylene protons of the O–CH₂CH₂–N group at 176.2 and 232.4 ppm, respectively (both 4 H). In respect to the higher electronegativity of oxygen relative to nitrogen the signal at 232.4 ppm is attributable to the O–CH₂ group, whereas the signal at 176.2 ppm has its origin in the N– CH₂ protons. The line width of these signals is much larger than those of the other signals of this spectrum.

Again line broadening for all signals can be observed with decreasing temperature (Fig. 8). This is most significant for all methylene protons, namely for the



Fig. 7. Temperature dependence of the chemical shifts in the ¹H NMR spectrum of $[{ybCp_2(\mu-OCH_2CH_2NEt_2)}_2]$ (3).



Fig. 8. Temperature dependence of the ¹H NMR signal widths in [{YbCp₂(μ -OCH₂CH₂NEt₂)}₂] (3).

N-CH₂-CH₃ group and for the two sets of protons of the O-CH₂-CH₂-N group. These are therefore the protons which are most affected by increased Yb-N interaction. It is interesting to note that with decreasing temperature the signals of the O-CH₂-CH₂-N protons are shifted to lower frequencies (upfield), whereas the signal for the methylene protons of the N-CH₂-CH₃ groups is shifted to higher frequencies (downfield) (Fig. 7). Again the line broadening for the methyl protons of the ethyl group is relatively small compared to the methylene protons. Also the chemical shift is fairly constant. The signal of the methyl protons shifts to slightly higher frequencies (downfield) at low temperature. This indicates that the methyl group is not significantly influenced by the increased interaction between Yb and N. The chemical shift for the Cp protons is also very constant, it is shifted to slightly lower frequencies (upfield) at lower temperatures. Seemingly, the Cp ligands are less affected by the increased interaction between Yb and N. This reflects also the line widening, which is much smaller than it is for the dimethylaminoalcoholato complex.

3. Conclusions

Treatment of [YbCp₃(thf)] with 2,6-di-*tert*-butylphenol, dimethylaminoethanol or diethylaminoethanol resulted in clean substitution of a Cp ligand with the alcoholato ligand yielding [YbCp₂(O-C₆H₃^{*t*}Bu₂-2,6)(thf)], [{YbCp₂(μ -OCH₂CH₂NMe₂)}₂] and [{YbCp₂ (μ -OCH₂CH₂NEt₂)}₂] · (thf)₂, respectively. The sterically demanding phenolato ligand stabilises a monomeric structure while for the bifunctional ligands, centrosymmetric dimers were isolated. Variable-temperature ¹H NMR studies showed that for the latter two compounds, there exists an equilibrium in solution between complexes found in the solid state and those where the N donor was not bound to Yb. This should allow the potential for catalysis in these formally coordinatively unsaturated compounds.

4. Experimental

All reactions were carried out under inert atmosphere such as argon or purified dinitrogen gas using Schlenk, vacuum line and glovebox techniques. All solvents were refluxed for several days over a sodium benzophenone mixture and were freshly distilled when required. All glassware was flamed out and purged with inert gas for several times before use. Dicyclopentadiene and alcohols were purchased from Aldrich Chemical Co. NaCp was synthesised from the reaction of sodium metal with an excess of freshly cracked CpH in thf. [YbCp₃(thf)] or [YbCp₃] [45] was prepared according to literature procedures. NMR experiments were performed using a Bruker AVANCE DRX 400 Spectrometer: ¹H NMR (400.13 MHz) in CDCl₃, standard TMS. FT-IR-Spectra were recorded between 400 and 4000 cm^{-1} using a Perkin-Elmer (System 2000) spectrometer.

4.1. Syntheses

4.1.1. Preparation of $[YbCp_2(O-C_6H_3^tBu_2-2,6)(thf)](1)$

[YbCp₂(O-C₆H₃'Bu₂-2,6)(thf)] was prepared by the addition of 2,6-di(*tert*-butyl)phenol (0.056 g, 0.27 mmol) in 5 mL thf to [YbCp₃(thf)] (0.12 g, 0.27 mmol) in thf (15 mL). After stirring at rt for 6 h, the red solution was filtered, concentrated and cooled to -15 °C giving (1) as a red powder. Recrystallisation from thf gave large red crystals of the title compound. Yield: 0.11 g (73%). IR (KBr; in cm⁻¹): $\tilde{v} = 3083$ w, 3021 w, 2962 s, 2909 m,

2874 w, 1426 m, 1403 m, 1261 s, 1097 s, 1018 s, 860 m, 802 s, 747 m, 402 m, 394 m, 386 m.

4.1.2. Preparation of $[{YbCp_2(\mu-OCH_2CH_2NMe_2)}_2]$ (2)

[YbCp₃(thf)] (0.17 g, 0.39 mmol) was dissolved in dried thf (15 mL). To this green solution was slowly added *N*,*N*-dimethyl-2-aminoethanol (0.039 ml, 0.39 mmol) in thf (5 mL). The resulting orange-yellow solution was stirred at room temperature for 2 h. The solution was concentrated to half its volume and cooled to -15 °C. Orange-yellow single crystals suitable for X-ray analysis deposited after several days. Yield: 0.10 g (68 %). Mp.: 185 °C (dec.). ¹H NMR (RT): δ –23.3 (10 H, C₅H₅), 58.7 (2 H, NCH₂), 64.6 (6 H, NCH₃), 75.7 (2 H, OCH₂) ppm. For VT ¹H NMR spectra see Figs. 5 and 6.

4.1.3. Preparation of $[{YbCp_2(\mu - OCH_2CH_2NEt_2)}_2] \cdot 3(thf)_2(3)$

In a similar manner to that described above [YbCp₃(thf)] (0.12 g, 0.27 mmol) was treated with *N*,*N*-diethyl-2-aminoethanol (0.036 ml, 0.27 mmol), yielding after similar work up orange-yellow crystals of the title compound. Yield 86%. ¹H NMR (RT) δ –56.3 (10 H, C₅H₅), 48.6 (6 H, NCH₂CH₃), 77.3 (4 H, NCH₂CH₃), 176.0 (2 H, NCH₂), 232.1 (2 H, OCH₂) ppm. For VT ¹H NMR spectra see Fig. 5 and 6. IR (KBr; in cm⁻¹): $\tilde{\nu} = 3092$ w, 2968 s, 2936 m, 2871 m, 2851 m, 2817 m, 1631 w, 1530 w, 1475 m, 1460 m, 1441 m, 1372 m, 1261 s, 1097 s, 1078 s, 1038 s, 1013 s, 916 m, 896 m, 780 s, 733 w, 590 w.

The thf-free complex $[{YbCp_2(\mu-OCH_2CH_2NEt_2)}_2]$ was obtained from $[YbCp_3]$ and *N*,*N*-diethyl-2-aminoethanol in toluene.

4.2. X-ray crystallography

All X-ray quality crystals were sealed and mounted in thin walled capillaries, with hemispheres of data collected at room temperature on a Bruker SMART 1000 CCD diffractometer, MoK_{α} radiation ($\lambda = 0.71073$ Å), using the omega scan mode with total reflections and unique data listed below. Data sets were corrected for absorption using the program SADABS [46]. Structures were solved using the Patterson method and refined on F^2 using SHELXL-97-2 [47] with X-SEED as the graphic interface [48]. All non-hydrogen atoms were located and were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (riding model) and were not refined. Details of the X-ray data collection and refinements appear below and selected bond lengths and angles are compiled in tables.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 223178–223180. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336-033; email: deposit@ccdc.cam.ac.uk).

5. Crystal refinement data

5.1. Crystal data for $C_{28}H_{39}O_2Yb$, (1)

 $M = 580.63, 0.26 \times 0.24 \times 0.12 \text{ mm}^3, \text{monoclinic},$ space group $P2_1/c$ (No. 14), a = 19.3429(13),b = 8.4363(6), c = 17.0342(12) Å, $\beta = 114.9220(10)^\circ,$ V = 2520.8(3) Å³, $Z = 4, D_c = 1.530 \text{ g/cm}^3, F_{000} = 1172,$ T = 296(2) K, 11,145 reflections collected, 3628 unique $(R_{\text{int}} = 0.0872)$. Final GooF = 1.007, $R_1 = 0.0411,$ $wR_2 = 0.0991, R$ indices based on 3130 reflections with $I > 2\sigma(I)$ (refinement on F^2), 286 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 3.731 \text{ mm}^{-1}$.

5.2. Crystal data for $C_{28}H_{40}N_2O_2Yb_2$, (2)

 $M = 782.70, 0.30 \times 0.20 \times 0.20 \text{ mm}^3$, monoclinic, space group C2/c (No. 15), a = 13.9757(12), b =9.3595(8), c = 21.0611(19) Å, $\beta = 103.008(2)^\circ$, V = 2684.2(4) Å³, $Z = 4, D_c = 1.937$ g/cm³, $F_{000} = 1512$, T = 296(2) K, 6000 reflections collected, 1935 unique ($R_{\text{int}} = 0.0552$). Final GooF = 1.058, $R_1 = 0.0361$, $wR_2 = 0.0957$, R indices based on 1535 reflections with $I > 2\sigma(I)$ (refinement on F^2), 154 parameters, 10 restraints. Lp and absorption corrections applied, $\mu = 6.952$ mm⁻¹.

5.3. Crystal data for $C_{20}H_{24}NO_3Yb$, (3)

 $M = 499.44, 0.30 \times 0.24 \times 0.22$ mm, orthorhombic, space group *Pnma* (No. 62), a = 9.5581(9), b = 30.572(3), c = 13.6722(13) Å, V = 3995.1(6) Å³, $Z = 8, D_c = 1.661$ g/cm³, $F_{000} = 1960$, Bruker SMART 1000 CCD diffractometer, MoK α radiation, $\lambda = 0.71073$ Å, T = 296(2)K, $2\theta_{max} = 46.6^{\circ}$, 17,483 reflections collected, 2942 unique ($R_{int} = 0.0553$). Final *GooF* = 1.155, $R_1 = 0.0414, wR_2 = 0.1083, R$ indices based on 2362 reflections with $I > 2\sigma(I)$ (refinement on F^2), 244 parameters, 36 restraints. Lp and absorption corrections applied, $\mu = 4.698$ mm⁻¹.

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