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Journal of Organometallic Chemistry 525 (1996) 247–254

Journal
of Organometallic
Chemistry

Organolanthanoids

XX¹. The synthesis of $\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$ (Cp = cyclopentadienyl; THF = tetrahydrofuran), $\text{YbCp}_2\text{X}(\text{THF})$ (X = Br or I), and $(\text{YbCp}_2\text{X})_2$ (X = Cl, Br, or I) by oxidation of YbCp_2 with metal and organic halides, and the determination of the X-ray crystal structure of $\text{YbCp}_2\text{I}(\text{THF})$

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Received 16 April 1996

Abstract

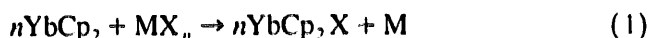
Reaction of $\text{YbCp}_2(\text{DME})$ (Cp = cyclopentadienyl; DME = 1,2-dimethoxyethane) with MCl_2 (M = Hg, Cd, Zn, Pb, Sn, Cu, Pd, or Co) or MCl (M = Ag, Cu or Tl) in tetrahydrofuran (THF) gives the metal M and $\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$, generally in excellent yield, with small amounts of TlCp and CoCp_2 also detected from TlCl and CoCl_2 respectively. Similarly, $\text{YbCp}_2\text{X}(\text{THF})$ (X = Br or I) and $\text{YbCp}_2\text{Cl}(\text{DME})_{0.5}$ have been prepared in good yields by analogous oxidation with suitable mercury(II) halides. However $\text{YbCp}_2(\text{DME})$ and FeCl_3 yield ferrocene. In simpler syntheses, $\text{YbCp}_2\text{X}(\text{THF})_n$ (X = Cl, n = 0.5; X = Br or I, n = 1) have been obtained by reactions of $\text{YbCp}_2(\text{DME})$ with C_2Cl_6 or $(\text{CH}_2\text{X})_2$ (X = Br or I) in THF, and $(\text{YbCp}_2\text{X})_2$ by analogous reactions of unsolvated YbCp_2 in petroleum ether. The X-ray crystal structure of $\text{YbCp}_2\text{I}(\text{THF})$ (monoclinic, $P2_1/c$, $a = 8.147(1)$, $b = 13.788(2)$, $c = 14.149(3)$ Å, $\beta = 105.56(1)^\circ$, $Z = 4$, $R = 0.042$, for 2324 observed data) shows the complex to be monomeric with formal eight coordination for ytterbium, and with a pseudo-tetrahedral array of the centroids of the Cp rings, oxygen, and iodine ($\langle \text{Yb}-\text{C} \rangle = 2.565$ Å, $\text{Yb}-\text{O} = 2.311(5)$ Å, $\text{Yb}-\text{I} = 2.9316(7)$ Å).

Keywords: Ytterbium; Cyclopentadienyl; Oxidation; Rare earth; Crystal structure; Lanthanide

1. Introduction

A wide range of ytterbium(III) and samarium(III) derivatives can be prepared by oxidation reactions of bis(cyclopentadienyl or substituted cyclopentadienyl)-lanthanoid compounds [2–4], with $\text{Sm}(\text{C}_5\text{Me}_5)_2$ a particularly rich source of new reactions [2–4]. Development of a simple, near quantitative synthesis of $\text{YbCp}_2(\text{DME})$ (Cp = cyclopentadienyl; DME = 1,2-dimethoxyethane) from ytterbium metal and thallium(I) cyclopentadienide [5,6] has made this compound readily

available for oxidation reactions. We have given a preliminary account of oxidations by a variety of metal salts and organometallics (reaction (1)) [7]



(generally M = Tl or Hg, n = 1 or 2; e.g. X = R, $\text{O}_2\text{CR}'$, halide, or $(\text{R}'\text{CO})_2\text{CH}$)

and have given a detailed account of oxidation syntheses of $\text{YbCp}_2(\text{O}_2\text{CR}')$ (e.g. R' = Me, Ph, CF_3 , C_6F_5 , pyridin-2-yl) [8] and YbCp_2R (R = C_6F_5 , C_6Cl_5 , or PhCC) [9] derivatives. A complete account is now provided of oxidation of YbCp_2 by a range of metal halides, together with new simple oxidations by organic halides which provide convenient access to the unsolvated dimers $(\text{YbCp}_2\text{X})_2$ (X = Cl, Br or I), and the X-ray crystal structure determination of $\text{YbCp}_2\text{I}(\text{THF})$.

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No structure of any simple LnCp_2I derivative has been published [2,3]. There are a few crystal structures of adducts of substituted bis(cyclopentadienyl)lanthanoid iodides, $\text{Ln}(\text{C}_5\text{R}_x\text{H}_{5-x})_2\text{I}(\text{L})_n$ [2,3], e.g. $\text{Sm}(\text{C}_5\text{Me}_5)_2\text{I}(\text{THF})$ [10], and of lanthanocene iodides with cyclopentadienyls containing methoxyethyl substituents, [2,3], e.g. $\text{Ln}(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{I}$ ($\text{Ln} = \text{Y}$, La , or Yb) [11].

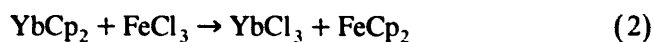
2. Results and discussion

2.1. Syntheses

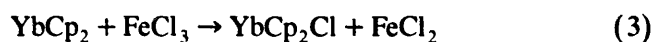
The reactions of $\text{YbCp}_2(\text{DME})$ with a range of metal halides are summarised in Table 1. The complexes $\text{YbCp}_2\text{X}(\text{L})_n$ ($\text{X} = \text{Cl}$, $\text{L} = \text{THF}$ or DME , $n = 0.5$; $\text{X} = \text{Br}$ or I , $\text{L} = \text{THF}$, $n = 1$) were prepared by reaction (1) ($n = 1$, $\text{M} = \text{Tl}$, Ag , or Cu , $\text{X} = \text{Cl}$; $n = 2$, $\text{M} = \text{Hg}$, Pd , Cu , Cd , Zn , Pb , Sn , Co , $\text{X} = \text{Cl}$; $n = 2$, $\text{M} = \text{Hg}$, $\text{X} = \text{Br}$ or I), generally in THF , but a typical reaction was also carried out in DME (Table 1) indicating that other media can be used. Yields were generally high to near quantitative, and where the amount of metal precipitated was determined (Table 1), these yields were near quantitative. Most reactions appeared instantaneous at room temperature, except with ZnCl_2 and CoCl_2 where there were induction times of 10 and 15 min respectively. Extended reaction times were used to ensure complete reactions, but were probably not needed as illustrated by the high yields obtained in typical reactions with HgCl_2 and TlCl using short times (Table 1).

From the reactions with TlCl and CoCl_2 , small amounts of TlCp and CoCp_2 were also obtained, whilst

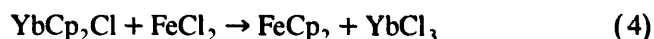
the reaction with FeCl_3 gave ferrocene as the major organometallic product.



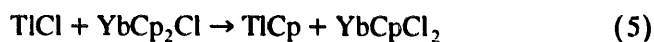
The formation of ferrocene is explicable in terms of initial oxidation of ytterbium to the usual YbCp_2Cl (reaction (3))



followed by cyclopentadienylation of iron(II) chloride by the ytterbium(III) organometallic (reaction (4)).



Similarly, formation of CoCp_2 and TlCp can be attributed to cyclopentadienylation of the metal chlorides by YbCp_2Cl , and the yield of TlCp increased with reaction time. Moreover, conversion of TlCl to TlCp by YbCp_2Cl has been independently demonstrated.



Redox potentials for $\text{M}^{2+} + 2\text{e}^- \rightarrow \text{M}$, $\text{M}^+ + \text{e}^- \rightarrow \text{M}$, and $\text{Yb}^{3+} + \text{e}^- \rightarrow \text{Yb}^{2+}$ in aqueous solution [12] indicate that the metal chlorides used should be able to oxidise $\text{Yb}(\text{II})$, as observed (Table 1). Values for $\text{YbCp}_3 + \text{e}^- \rightarrow \text{YbCp}_3^-$ [13] and $\text{Yb}(\text{C}_5\text{Me}_5)_2 + \text{e}^- \rightarrow \text{Yb}(\text{C}_5\text{Me}_5)_2^-$ [14] indicate that divalent organoytterbium species are ca. 1.0 V more powerful reductants than aqueous Yb^{2+} , but 0.4 V is due to differences in reference electrodes. Correspondingly it may also be that the metal halides are more difficult to reduce in THF than in water.

The reactions of $\text{YbCp}_2(\text{DME})$ with the organic oxidants hexachloroethane and 1,2-dibromo- and 1,2-diiodoethane are summarised in Table 2. Oxidation pro-

Table 1
Oxidation reactions of $\text{YbCp}_2(\text{DME})$ with metal salts

$\text{YbCp}_2(\text{DME})$ (mmol)	Metal salt (mmol)	THF (ml)	Reaction time (h) ^a	Product YbCp_2X	Yield (%)	Other products (% yield)
3.30	HgCl_2 (1.54)	20	16	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	96	Hg (90)
1.71	HgCl_2 (0.80)	20	0.5	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	90	
2.71	HgCl_2 (1.35)	15 ^b	16	$\text{YbCp}_2\text{Cl}(\text{DME})_{0.5}$	100	
3.30	PdCl_2 (1.54)	30	16	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	71	
2.36	AgCl (2.32)	30	16	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	89	
1.54	CuCl (1.54)	20	16	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	98	
1.85	CuCl_2 (0.89)	25	16	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	81	
2.96	CuCl_2 (1.46)	20	16	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	80	Cd (100)
1.93	ZnCl_2 (0.98)	30	72	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	83	
2.11	PbCl_2 (1.04)	20	16	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	80	Pb (100)
2.20	SnCl_2 (1.10)	20	48	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	96	
1.69	TlCl (1.65)	20	1	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	94	TlCp (3)
1.69	TlCl (1.65)	20	16	^c		TlCp (5)
1.64	CoCl_2 (0.93)	30	72	$\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$	45	CoCp_2 (1)
2.02	FeCl_3 (2.05)	20	48			FeCp_2 (60)
3.53	HgBr_2 (1.71)	15	16	$\text{YbCp}_2\text{Br}(\text{THF})$	71	Hg (94)
3.31	HgI_2 (1.63)	15	16	$\text{YbCp}_2\text{I}(\text{THF})$	73	Hg (92)

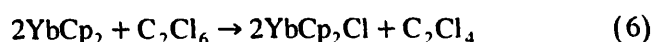
^a At room temperature. ^b DME . ^c Not investigated.

Table 2
Oxidation reactions of YbCp₂(DME) with organic halides

YbCp ₂ (DME) (mmol)	Organic halide (mmol)	THF (ml)	Reaction time (h) ^a	Product YbCp ₂ X	Yield (%)
1.91	C ₂ Cl ₆ (0.95)	15	3	YbCp ₂ Cl(THF) _{0.5}	58
1.65	(BrCH ₂) ₂ (1.16)	15	3	YbCp ₂ Br(THF)	55
1.98	(ICH ₂) ₂ (0.99)	20	3	YbCp ₂ I(THF)	64
2.20	C ₂ Cl ₆ (1.14)	15 ^b	24	(YbCp ₂ Cl) ₂	70
2.11	(BrCH ₂) ₂ (1.39)	15 ^b	24	(YbCp ₂ Br) ₂	79
1.71	(ICH ₂) ₂ (0.85)	15 ^b	24	(YbCp ₂ I) ₂	87

^a At room temperature. ^b Petroleum ether.

ceeded straightforwardly in THF to give YbCp₂Cl(THF)_{0.5} and YbCp₂X(THF) (X = Br or I) in good yield (reactions (6) and (7)).



These syntheses are simpler than the oxidations with metal salts (reaction (1)) which require a filtration step to remove precipitated metal, since the organic product is either a gas or is soluble in petroleum ether (C₂Cl₄) providing easy separation from YbCp₂Cl(THF)_{0.5}. This difference parallels the recent simplification of the synthesis of LnCl₃(THF)_n complexes from Ln metal by using C₂Cl₆ [15] rather than HgCl₂ [16] as the oxidant. Unsolvated (YbCp₂X)₂ derivatives have also been prepared by carrying out reactions (6) and (7) in petroleum ether. Extended reaction times were used to ensure complete oxidation as both the reactant, unsolvated YbCp₂, and the (YbCp₂X)₂ products are insoluble in petroleum ether. These reactions also reveal the superiority of reactions (6) and (7) over reaction (1) as a route to YbCp₂X complexes, since even if (1) could be effected in petroleum ether, the metal and the organometallic product would be coprecipitated. Oxidation syntheses (1), (6) and (7) have a major advantage over metathesis syntheses (from YbX₃ and alkali metal cyclopentadienides) of ytterbocene halides [2,3] in that the products are obtained free of alkali metal halides.

2.2. Characterization of YbCp₂X(L)_n and (YbCp₂X)₂ complexes

The dimeric structures of unsolvated ytterbocene chloride and bromide have been established by X-ray crystallography [17,18]. There are two closely related forms of each, one with a centrosymmetric dimer and the other with similar centro- and non-centrosymmetric dimers in a 1:2 ratio [17,18]. The compositions of the present unsolvated halogenobis(cyclopentadienyl)ytterbium(III) compounds were established by ytterbium analyses, and the dimeric nature was consistent with detection of [(YbCp₂X)₂]⁺ parent ions and other bimolecular species in their mass spectra. Two halogen-

mass sensitive bands are observed in the far infrared spectrum of each complex (Table 3), as expected for $\nu(\text{Yb-X})$ of (YbCp₂X)₂. The ratios of $\langle \nu(\text{Yb-Br}) \rangle / \langle \nu(\text{Yb-Cl}) \rangle$ (0.70) and $\langle \nu(\text{Yb-I}) \rangle / \langle \nu(\text{Yb-Cl}) \rangle$ (0.54) are consistent with this assignment [19]. Our absorption frequencies for (YbCp₂Cl)₂ are in agreement with those reported earlier for unsolvated YbCp₂Cl [20], for which $\nu(\text{Yb-Cl})$ was not assigned, whilst the earlier assignment [20] of a band near 250 cm⁻¹, and now also that at 276–271 cm⁻¹, to $\nu(\text{Yb-C})$ is supported by the invariance of these bands to change of halogen. The correlation of the far infrared spectrum of ytterbocene iodide with those of the X-ray characterized [17,18] bromide and chloride indicates that the iodide is also dimeric.

The composition of the complexes YbCp₂X(L)_n (X = Cl, L = THF or DME, n = 0.5; X = Br or I, L = THF, n = 1) was supported by C, H, Yb, and generally halogen analyses, although the C, H figures for YbCp₂X(THF) (X = Br or I) deviated from calculated values by 1–2%, a not infrequent occurrence in organolanthanoid chemistry (for recent examples see Ref. [21]). We have previously observed the composition YbCp₂Cl(THF)_{0.5} for the product from the reaction of YbCp₂(DME) with Hg(*trans*-CCl=CCl₂)₂ [9], and it is supported by several separate analyses in the present case (see Experimental section), but it is in contrast to the composition YbCp₂Cl(THF) observed by others [22–24] (the composition of 'in situ' YbCp₂Cl(THF) [24] was assumed from Ref. [23]). The present products were dried for prolonged periods under vacuum, sometimes with warming. All solvates gave [(YbCp₂X)₂]⁺ and

Table 3
Far infrared spectra of YbCp₂X(THF)_n and (YbCp₂X)₂ complexes

Complex	IR absorption bands (300–100 cm ⁻¹) ^a
(YbCp ₂ Cl) ₂	273s, 253m, 222s , 206s
(YbCp ₂ Br) ₂	276s, 244m, 155s , 146s
(YbCp ₂ I) ₂	271s, 242m, 125s , 108m
YbCp ₂ Cl(THF) _{0.5}	273s, 262s, 222m , 201m
YbCp ₂ Br(THF)	262s, 243m(sh), 178s , 158m (sh)
YbCp ₂ I(THF)	264s, 245m(sh), 168w , 136m , 119w

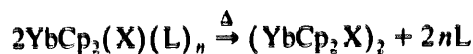
^a Frequencies in bold are assigned to $\nu(\text{Yb-X})$.

Table 4
Atomic coordinates and equivalent isotropic displacement coefficients for $\text{YbCp}_2\text{I}(\text{THF})$

Atom	x	y	z	$U_{\text{eq}} (\text{\AA}^2)^a$
Yb	0.2081(1)	0.1045(1)	0.1970(1)	0.047(1)
I(1)	0.2917(1)	-0.0902(1)	0.1407(1)	0.090(1)
O(1)	0.4350(7)	0.1033(3)	0.3361(4)	0.062(1)
C(1)	0.4072(15)	0.2295(9)	0.1487(8)	0.098(4)
C(2)	0.3816(15)	0.1643(9)	0.0811(9)	0.099(3)
C(3)	0.2110(21)	0.1663(12)	0.0273(7)	0.128(6)
C(4)	0.1367(14)	0.2383(13)	0.0681(14)	0.134(6)
C(5)	0.2603(20)	0.2766(7)	0.1408(11)	0.116(4)
C(6)	0.0296(16)	0.0385(14)	0.3088(11)	0.127(6)
C(7)	-0.0582(16)	0.0186(10)	0.2191(12)	0.110(4)
C(8)	-0.1136(14)	0.1001(14)	0.1718(10)	0.126(6)
C(9)	-0.0598(19)	0.1742(9)	0.2341(19)	0.144(7)
C(10)	0.0286(16)	0.1366(18)	0.3166(11)	0.166(10)
C(11)	0.5940(11)	0.0589(11)	0.3433(8)	0.114(4)
C(12)	0.6989(13)	0.0721(13)	0.4408(8)	0.113(4)
C(13)	0.6274(12)	0.1442(9)	0.4858(8)	0.102(3)
C(14)	0.4555(10)	0.1674(6)	0.4201(6)	0.075(2)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

other dinuclear ions in the mass spectra, but this does not necessarily establish the presence of dimers in the solid state, since this is observed for the X-ray established (below) monomeric $\text{YbCp}_2\text{I}(\text{THF})$. Transformation of the solvates into dimers is likely upon heating



despite a report of unchanged sublimation of solvates [2].

The far infrared spectrum of $\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$ is very similar to that of $(\text{YbCp}_2\text{Cl})_2$, with two $\nu(\text{Yb}=\text{Cl})$ frequencies as expected for a halogen bridged dimer. Accordingly, the product is considered to be a dimer, and THF is probably solvent of crystallization. Nevertheless, coordination to one Yb giving one nine and one eight coordinate metal cannot be ruled out, since crystal

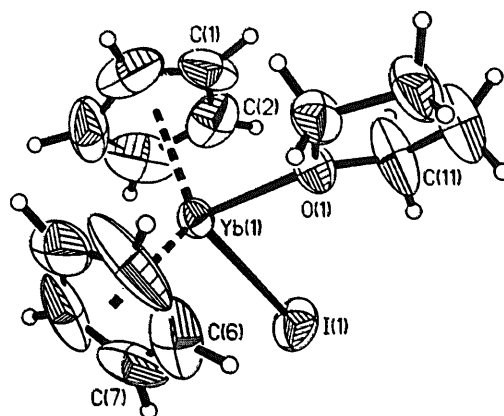


Fig. 1. The molecular structure of $\text{YbCp}_2\text{I}(\text{THF})$.

structures of nine coordinate $[\text{LnCp}_2\text{Cl}(\text{THF})]_2$ are known [25], for both larger ($\text{Ln} = \text{Nd}$) and smaller ($\text{Ln} = \text{Er}$) lanthanoids. However this would be expected to lower $\nu(\text{Yb}=\text{Cl})$ from values for $(\text{YbCp}_2\text{Cl})_2$. $\text{YbCp}_2\text{Cl}(\text{DME})_{0.5}$ is also considered to be a solvated dimer. Both $\text{YbCp}_2\text{X}(\text{THF})$ ($\text{X} = \text{Br}$ or I) complexes have single $\nu(\text{Yb}=\text{X})$ frequencies (Table 3), consistent with eight coordinate monomers, as established for $\text{X} = \text{I}$ (below). These absorptions are at higher energies than observed for the corresponding dimers (Table 3), consistent with the expected relationship between metal-halogen stretching frequencies of terminal and bridging metal-halogen bonds.

2.3. The X-ray structure determination of $\text{YbCp}_2\text{I}(\text{THF})$

The atomic coordinates for $\text{YbCp}_2\text{I}(\text{THF})$ are listed in Table 4, selected bond distances and angles in Table 5, and the molecular structure is displayed in Fig. 1. The compound is monomeric with formal eight coordination and pseudo-tetrahedral stereochemistry (O, I, and the centroids (cen(1), (2)) of the cyclopentadienyl ligands) for ytterbium. Thus, the structure is similar to that

Table 5
Selected bond distances and angles for $\text{YbCp}_2\text{I}(\text{THF})$

Bond	Distance (Å)	Bond	Distance (Å)
Yb(1)–O(1)	2.311(5)	Yb(1)–I(1)	2.9316(7)
Yb(1)–C(1)	2.581(8)	Yb(1)–C(6)	2.585(9)
Yb(1)–C(2)	2.571(8)	Yb(1)–C(7)	2.564(9)
Yb(1)–C(3)	2.554(9)	Yb(1)–C(8)	2.550(11)
Yb(1)–C(4)	2.549(9)	Yb(1)–C(9)	2.565(11)
Yb(1)–C(5)	2.575(10)	Yb(1)–C(10)	2.555(10)
Yb(1)–cen(1) ^a	2.306	Yb(1)–cen(2) ^b	2.301
Angle	(deg)	Angle	(deg)
O(1)–Yb(1)–I(1)	91.96(12)	cen(1) ^a –Yb(1)–cen(2) ^b	129.8
O(1)–Yb(1)–cen(1) ^a	105.7	I(1)–Yb(1)–cen(1) ^a	108.3
O(1)–Yb(1)–cen(2) ^b	106.4	I(1)–Yb(1)–cen(2) ^b	108.2

^a cen(1) is the centroid of the Cp ring C(1)–C(5).

^b cen(2) is the centroid of the Cp ring C(6)–C(10).

of $\text{LuCp}_2\text{Cl}(\text{THF})$ [26]. However, in the latter $\langle \text{Ln}-\text{C} \rangle$ differs for the two Cp rings (2.58, 2.54 Å), whereas $\langle \text{Yb}-\text{C} \rangle$ is essentially the same for the two rings of the present structure. Subtraction of the ionic radius for eight coordinate Ln^{3+} [27] from $\langle \text{Ln}-\text{C} \rangle$ for the complexes gives 1.58 Å for $\text{Ln} = \text{Yb}$, intermediate between the values (1.61, 1.56 Å) for the two rings of $\text{LuCp}_2\text{Cl}(\text{THF})$. These values are as expected [28] for a cyclopentadienyl 'ionic radius', $\text{Yb}-\text{O}$ is typical for $\text{Ln}-\text{O}(\text{THF})$ in a relatively uncrowded environment and is similar to $\text{Lu}-\text{O}$ (2.27(1) Å) of $\text{LuCp}_2\text{Cl}(\text{THF})$ [26]. Subtraction of the Ln^{3+} ionic radius gives 1.33 Å, which is close to values (1.34 ± 0.05 Å) for a range of uncrowded $\text{Ln}-\text{O}(\text{THF})$ complexes [29], e.g. 1.29 Å for $\text{LuCp}_2\text{Cl}(\text{THF})$ [26] and 1.37 Å for $\text{Sm}(\text{C}_5\text{Me}_5)_2\text{I}(\text{THF})$ [10], and is much less than values (1.49–1.59 Å) for complexes with substantial steric crowding [30]. As expected, $\text{Yb}-\text{I}$ of $\text{YbCp}_2\text{I}(\text{THF})$ (Table 5) is shorter than that (3.049(1) Å) in formally nine coordinate $\text{Yb}(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{I}$ [11], but the difference (0.12 Å) is larger than expected from the ionic radii difference (0.06 Å) [27]. Subtraction of the appropriate Yb^{3+} ionic radii gives 1.95 and 2.01 Å respectively, and the value for $\text{YbCp}_2\text{I}(\text{THF})$ is similar to that (1.97 Å) derived from $\text{Sm}-\text{I}$ of $\text{Sm}(\text{C}_5\text{Me}_5)_2\text{I}(\text{THF})$ [10] and 1.98 Å from $\text{Y}-\text{I}$ of $\text{Y}(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{I}$ [11]. The $\text{cen}(1)-\text{Yb}-\text{cen}(2)$ and $\text{O}-\text{Yb}-\text{I}$ angles (Table 5) are similar to corresponding values of $\text{LuCp}_2\text{Cl}(\text{THF})$ (129 and 91.6(4)° respectively) [26], hence there is no contraction of $\text{cen}-\text{Ln}-\text{cen}$ owing to introduction of the larger halogen.

3. Experimental

3.1. General remarks

All the ytterbium complexes are extremely air and moisture sensitive. Thus, all reactions and manipulations of these compounds were carried out under purified nitrogen or argon, using Schlenk, vacuum line and drybox techniques. Analytical and spectroscopic methods and instrumentation were generally as described previously [31]. IR spectra ($4000-650\text{ cm}^{-1}$) listed below were obtained for compounds in dry Nujol. Far infrared spectra ($650-100\text{ cm}^{-1}$) of complexes were obtained as Vaseline mulls between polyethylene plates with a Bruker IFS 120 HR spectrometer. Bands are listed only for the region $300-100\text{ cm}^{-1}$ (Table 3), as there were no significant absorptions at $650-300\text{ cm}^{-1}$. In listed mass spectra, each m/z value corresponds to the main peak of a cluster with the appropriate isotope pattern. In addition to the listed m/z values, each spectrum revealed features attributable to ions containing halogens different from that of the oxidant, e.g. $\text{YbCp}_2\text{Br}(\text{THF})$ gave m/z 722 ($\text{Yb}_2\text{Cp}_4\text{BrCl}^+$). This

can be attributed to halogen exchange in the spectrometer source, a phenomenon well known for halogenomercury compounds [32]. Molar extinction coefficients are approximate for solutions of $(\text{YbCp}_2\text{X})_2$ in benzene owing to the low solubility of the compounds in this solvent.

Solvent, nitrogen, and argon purification have been given previously [31]. Petroleum ether has b.p. 60–70°C for method 1 and 40–60°C for methods 2 and 3. Ytterbium powder was from Rhone-Poulenc, Phoenix, AZ, and thallium(I) cyclopentadienide was prepared by the reported method [33]. Most metal halides were standard commercial anhydrous samples and were used without purification. Cobalt(II) chloride hexahydrate was dehydrated at 150°C under vacuum. Hexachloroethane was sublimed before use, 1,2-dibromoethane was dried over molecular sieves for two days and distilled under nitrogen, and 1,2-diiodoethane was freshly recrystallized from diethyl ether. Biscyclopentadienyl-1,2-dimethoxyethanytterbium(II) was prepared by the reported method [5,6]. The desolvated complex YbCp_2 was obtained by desolvation of $\text{YbCp}_2(\text{THF})_2$ [34], which was synthesized by redox transmetalation [5].

3.2. Syntheses of bis(cyclopentadienyl)halogenoytterbium(III) complexes

3.2.1. Method 1: oxidation of $\text{YbCp}_2(\text{DME})$ by metal halides

Amounts of reagents, solvent volumes, reaction times and yields of products are given in Table 1. To stoichiometric amounts of $\text{YbCp}_2(\text{DME})$ and the metal halide was added THF or in one case DME under purified nitrogen. Reaction was generally instantaneous (for exceptions see Section 2.1) giving an orange solution and a metal precipitate. After stirring at room temperature, the reaction mixture was filtered, the filter was washed at least twice with the reaction solvent, and the filtrate was evaporated to dryness under vacuum. The resulting orange product was dried under vacuum for 2–3 h (10^{-3} mm Hg) with occasional warming. Lead and cadmium were deposited as metallic pieces which could readily be removed from the Celite filter pad and weighed. For determination of mercury, the filter and the Celite pad were treated with a mixture of concentrated nitric and sulfuric acids and the resulting mixture digested until a clear solution was obtained. The mercury was then determined gravimetrically as HgS [35].

3.2.2. Method 2: oxidation of $\text{YbCp}_2(\text{DME})$ with haloalkanes in THF

Amounts of reagents, solvent volumes, reaction times and yields of products are given in Table 2. On mixing the required amounts of $\text{YbCp}_2(\text{DME})$ and the haloalkane in the drybox, reaction was observed giving an orange product. THF was then added giving an

orange or red (with $(\text{CH}_2\text{I})_2$) solution, which was stirred at room temperature. The solvent was then removed under vacuum until crystallization of $\text{YbCp}_2\text{X}(\text{THF})_n$ began. The concentrated solution was stirred vigorously whilst petroleum ether was added, precipitating further product. The mixture was filtered under vacuum, and the product was washed twice with petroleum ether (10 ml). After all solvent from the filtrate was evaporated, the solid on the filter was dried under vacuum at room temperature for 7 h.

3.2.3. Method 3: oxidation of YbCp_2 with haloalkanes in petroleum ether

Amounts of reagents, solvent volumes, reaction times and yields of products are given in Table 2. Addition of the haloalkane to YbCp_2 in the drybox resulted in immediate reaction. Petroleum ether was then added and the reaction mixture stirred at room temperature giving an orange or brown suspension, which was filtered off and the solid washed twice with petroleum ether. After evaporation of the filtrate, the solid on the filter was dried for 3 h at room temperature under vacuum.

3.3. Properties of bis(cyclopentadienyl)halogenoytterbium(III) complexes

The complexes $\text{YbCp}_2\text{X}(\text{THF})_n$ were prepared by both methods 1 and 2. Similar spectroscopic properties were observed where the same compound was obtained by more than one method or from several metal halides.

3.3.1. Chlorobis(cyclopentadienyl)ytterbium(III)-tetrahydrofuran (2:1)

Anal. Found (method 1 using HgCl_2): C, 37.4, 38.5, 38.8; H, 3.6, 5.3, 5.7; Cl, 9.5; Yb, 45.0, 46.2, (45.4 from method 2). $\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{OYb}_2$ Calc.: C, 38.5; H, 3.8; Cl, 9.5; Yb, 46.2 cf. $\text{C}_{14}\text{H}_{18}\text{ClOYb}$ ($\text{YbCp}_2\text{Cl}(\text{THF})$) Calc.: C, 40.9; H, 4.4; Cl, 8.6; Yb, 42.1%. IR: ν 3070w, 2711w, 1560w(br), 1347w, 1248w, 1176w, 1041(sh)w, 1011s, 921w, 854m, 784vs, 740(sh)w, 671w cm^{-1} . MS: m/z 678 [8, $(\text{YbCp}_2\text{Cl})^+$]; 613 [18, $\text{Yb}_2\text{Cp}_2\text{Cl}_2^+$]; 548 [3, $\text{Yb}_2\text{Cp}_2\text{Cl}_2^+$]; 483 [2, $\text{Yb}_2\text{CpCl}_2^+$]; 339 [2, YbCp_2Cl^+]; 304 [88, YbCp_2^+]; 239 [100, YbCp^+]; 209 [20, YbCl^+]; 174 [10, Yb^+]; 66 [46, CpH^+]; 65 [42, Cp^+]. Vis-near IR [λ_{max} (e)] (THF): 374(275), 875(2), 924(3), 949(11), 984(9), 993(24), 1004(2) nm ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

3.3.2. Bromobis(cyclopentadienyl)(tetrahydrofuran)ytterbium(III)

Anal. Found (method 1): C, 35.7; H, 3.8; Br, 18.4; Yb, 38.4 (39.1 from method 2). $\text{C}_{14}\text{H}_{18}\text{BrOYb}$ Calc.: C, 36.9; H, 4.0; Br, 17.6; Yb, 38.0%. IR: ν 3076w, 2711w, 1346m, 1247w, 1176w, 1040w, 1009s, 919w, 1560w(br), 873(sh)w, 853m, 804(sh)w, 786vs,

735(sh)w, 675w cm^{-1} . MS: m/z 766 [5, $(\text{Cp}_2\text{YbBr})^+$]; 701 [10, $\text{Yb}_2\text{Cp}_3\text{Br}_2^+$]; 636 [3, $\text{Yb}_2\text{Cp}_2\text{Br}_2^+$]; 571 [1, Yb_2CpBr^+]; 383 [4, YbCp_2Br^+]; 318 [4, YbCpBr^+]; 304 [87, YbCp_2^+]; 253 [28, YbBr^+]; 239 [100, YbCp^+]; 174 [14, Yb^+]; 65 [75, Cp^+]. Vis-near IR [λ_{max} (e)] (THF): 380(230), 876(1), 923(2), 952(13), 985(8), 995(18), 1006(1) nm ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

3.3.3. Bis(cyclopentadienyl)iodo(tetrahydrofuran)ytterbium(III)

Anal. Found (method 1): C, 32.1; H, 3.5; I, 25.0; Yb, 34.5 (34.6 from method 2). $\text{C}_{14}\text{H}_{18}\text{IOYb}$ Calc.: C, 33.5; H, 3.6; I, 25.3; Yb, 34.5%. IR: ν 3079w, 2710w, 1346m, 1247w, 1177w, 1038w, 1008s, 923w, 850m, 1560w(br), 804(sh)s, 788vs, 728(sh)w cm^{-1} . MS: m/z 860 [4, $(\text{YbCp}_2\text{I})^+$]; 795 [4, $\text{Yb}_2\text{Cp}_3\text{I}_2^+$]; 733 and 730 overlapping, [2, $\text{Yb}_2\text{Cp}_4\text{I}^+$ and $\text{Yb}_2\text{Cp}_2\text{I}_2^+$]; 665 [1, $\text{Yb}_2\text{CpI}_2^+$]; 600 [1, Yb_2I_2^+]; 431 [9, YbCp_2I^+]; 366 and 365 overlapping [2, YbCpI^+ and $\text{YbC}_5\text{H}_4\text{I}^+$]; 304 [88, YbCp_2^+]; 239 [100, YbCp^+]; 174 [18, Yb^+]; 128 [10, HI^+]; 66 [74, CpH^+]; 65 [67, Cp^+]. Vis-near IR [λ_{max} (e)] (THF): 381(330), 879(2), 924(4), 956(27), 987(12), 998(27), 1010(2) nm ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

3.3.4. Chlorobis(cyclopentadienyl)ytterbium(III)-1,2-dimethoxyethane (2:1)

Anal. Found (method 1): C, 37.0; H, 2.5; Yb, 44.1, 44.6. $\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{O}_2\text{Yb}_2$ Calc.: C, 37.6; H, 3.9; Yb, 45.1%. IR: ν 3090w, 3070w, 2920w, 2840w, 2705w, 1440w, 1192w, 1050(sh)m, 1015s, 905w, 862w, 790s, 730m cm^{-1} . MS: similar to that of $\text{YbCp}_2\text{Cl}(\text{THF})_{0.5}$ except for observation of m/z 90 (3, DME^+). Vis-near IR: similar to that of the corresponding THF solvate.

3.3.5. Di(μ -chlorobis(cyclopentadienyl)ytterbium(III))

Anal. Found: Yb, 50.5. $\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{Yb}_2$ Calc.: Yb, 51.1%. IR: ν 3076w, 2710w, 1560w(br), 1011s, 783vs, 680w cm^{-1} . MS: m/z 678 [8, M^+]; 613 [19, $(\text{M}-\text{Cp})^+$]; 548 [4, $(\text{M}-2\text{Cp})^+$]; 483 [3, $(\text{M}-3\text{Cp})^+$]; 418 [1, $(\text{M}-4\text{Cp})^+$]; 339 [2, YbCp_2Cl^+]; 304 [90, YbCp_2^+]; 239 [100, YbCp^+]; 209 [24, YbCl^+]; 174 [12, Yb^+]; 66 [62, CpH^+]; 65 [52, Cp^+]. Vis-near IR [λ_{max} (e)] (benzene): 397(609), 946(41), 983(34), 997(22) nm ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

3.3.6. Di(μ -bromobis(cyclopentadienyl)ytterbium(III))

Anal. Found: Yb, 45.4. $\text{C}_{10}\text{H}_{10}\text{Br}_2\text{Yb}_2$ Calc.: Yb, 45.2%. IR: ν 3103w, 2709w, 1560w(br), 1121w, 1010s, 919w, 845w, 785vs cm^{-1} . MS: m/z 766 [4, M^+]; 701 [8, $(\text{M}-\text{Cp})^+$]; 636 [2, $(\text{M}-2\text{Cp})^+$]; 571 [1, $(\text{M}-3\text{Cp})^+$]; 383 [4, YbCp_2Br^+]; 318 [4, YbCpBr^+]; 304 [64, YbCp_2^+]; 253 [21, YbBr^+]; 239 [73, YbCp^+]; 174 [10, Yb^+]; 66 [100, CpH^+]. Vis-near IR [λ_{max} (e)] (benzene): 399(745), 949(42), 985(38), 998(21) nm ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

3.3.7. Di(bis(cyclopentadienyl)- μ -iodoytterbium(III))

Anal. Found: Yb, 40.6%. $C_{10}H_{10}I_2Yb_2$ Calc.: Yb, 40.2%. IR: ν 3094w, 2711w, 1010s, 892w, 786s(br) cm^{-1} . MS: m/z 860 [2, M^+]; 795 [2, (M-Cp) $^+$]; 733 and 730 overlapping, [1, (M-I) $^+$ and (M-2Cp) $^+$]; 665 [0.5, (M-3Cp) $^+$]; 600 [0.5, (M-4Cp) $^+$]; 431 [3, $YbCp_2I^+$]; 366 and 365 overlapping [1, $YbCpI^+$ and $YbC_5H_4I^+$]; 304 [33, $YbCp_2^+$]; 239 [40, $YbCp^+$]; 174 [6, Yb^+]; 128 [13, HI^+]; 66 [100, CpH^+]; 65 [89, Cp^+]. Vis-near IR [λ_{max} (e)] (benzene): 380br(990), 951(37), 984(34), 998(28) nm ($dm^3 mol^{-1} cm^{-1}$).

3.4. X-ray structure determination

3.4.1. Crystal refinement data

$C_{14}H_{18}IOYb$; $M = 502.22$; monoclinic; space group $P2_1/c$ (C_{2h}^5 ; No. 14); $a = 8.1473(13)$, $b = 13.788(2)$ and $c = 14.149(3)$ Å; $\beta = 105.558(13)^\circ$; $U = 1531.2(4)$ Å 3 ; $D_c = 2.179$ g cm^{-3} ; $Z = 4$; $F(000) = 932$; $\mu_{Mo} = 7.719$ mm $^{-1}$; specimen size $0.4 \times 0.4 \times 0.2$ mm 3 ; the crystal was mounted in a 0.5 mm diameter glass capillary under a dry argon atmosphere in the drybox; colour orange-red; $N = 11695$; $N_o = 2324$, $R_1 = 0.0417$, $wR_2 = 0.1079$; $n_v = 155$; $T = 293(2)$ K. Other specific procedural details: reflection weights $\omega = [\sigma^2(F_o)^2 + 0.0819P]^2$ where $P = (F_o^2 + 2F_c^2)/3$; measured on a Stoe imaging plate diffraction system; software SHELX93.

3.4.2. Structure determination

A unique data set was measured within the limit $4.2 \leq 2\theta \leq 48.5^\circ$; monochromatic Mo $K\alpha$ ($\lambda = 0.71073$ Å) was employed. N independent reflections were obtained (see above), N_o with $I > 2\sigma$ being considered 'observed' and used in the full-matrix least-squares refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_{H}$ were constrained at appropriate values. Residuals R_1 ($R_1 = \sum |F_o| - |F_c| / \sum |F_o|$) and wR_2 ($wR_2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2])^{1/2}$) are quoted at convergence. Neutral atom complex scattering factors were employed [36]. Atomic coordinates are given in Table 4, the structure is displayed in Fig. 1, and selected bond distances and angles are given in Table 5. Complete list of bond distances and angles, thermal parameters and hydrogen atom coordinates are available from the Cambridge Crystallographic Data Centre.

Acknowledgements

We are grateful to the Australian Research Council for support, and to M. Braun Garching for travel support for the visit of Dirk Steinfeldt to Monash University.

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