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# Metal-bridging versus chelating $Me_2Si(C_5H_4)_2$-ligands in binuclear complexes

## II *. The crystal structures of $[Me_2Si(C_5H_4)_2Yb(\mu\text{-}Br)]_2$ and non-sublimed $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$

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### Abstract

$YbBr_3$ reacts with $Na_2[Me_2Si(C_5H_4)_2]$ (1:1) to afford the new dimer, Si,Si,Si′,Si′-tetramethyldisila[1.1]ytterbocenophane dibromide, $[Me_2Si(C_5H_4)_2Yb(III)(\mu\text{-}Br)]_2$ (**4**), the structure of which was determined by a low-temperature crystallographic X-ray study. Complex **4** is isostructural with its analogue that contains Cl instead of Br. Simple model calculations have led to some predictions about the relative stabilities (depending on the nature of M and X) of the two $[Me_2Si(\eta^5\text{-}C_5H_4)_2M(\mu\text{-}X)]_2$ isomers with metal-bridging and chelating $Me_2Si(C_5H_4)_2$ ligands, respectively. The calculations indicate that the structurally undistorted $\{Me_2Si(C_5H_4)_2\}^{2-}$ anion is very poorly suited for metal coordination in either isomer. From solutions of $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$ (**1a**), crystals of the so far unreported modification **1a′** of this dimer were obtained, and its $[(C_5H_5)_2Sc(\mu\text{-}Cl)]_2$-like crystal structure was determined.

## Introduction

Two units of doubly deprotonated dimethyldicyclopentadienylsilane, $\{Me_2Si(C_5H_4)_2\}^{2-}$ (DMCS), and probably numerous derivatives thereof, should in principle be able to combine with a planar $\{M_2(\mu\text{-}X)_2\}^{4-}$ fragment (M = transition metal; X = e.g. halide, alkyl, hydride etc.) to afford two different isomers of the composition $[Me_2Si(\eta^5\text{-}C_5H_4)_2M(\mu\text{-}X)]_2$ (Fig. 1) [1]. Even a brief inspection of the geometry, however, indicates that the DMCS dianion would usually be unable to

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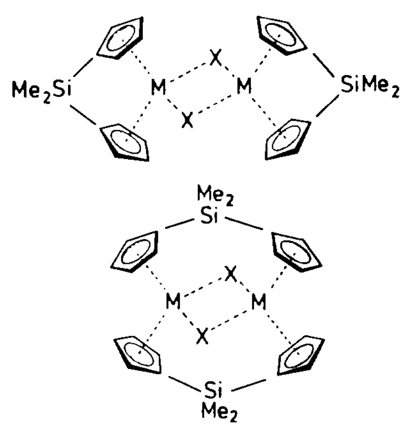

Fig. 1. Possible isomers of $[Me_2Si(C_5H_4)_2M(\mu\text{-}X)]_2$. Top: isomer I (with chelating DMCS ligands); bottom: isomer II (with metal bridging DMCS ligands).

coordinate satisfactorily in either of the two modes if the C(Cp)–Si–C(Cp)′ and Cent–C(Cp)–Si angles (i.e. $\alpha$ and $\beta$, respectively; Cent = center of a five-membered ring) have the usual values of 109.5 and 180°. Thus Fig. 2a shows that for a given metal ion $M^{n+}$, and with $\alpha = 110°$ and $\beta = 180°$, the M–Cent separation for isomer I would significantly exceed the optimal M–Cent distance, while for isomer II, in which the distance M–Cent can adopt its "natural" value, the usually rather short separation M ··· M′ would not represent a realistic M ··· M′ distance for a planar $M_2(\mu\text{-}X)_2$ fragment. In accordance with numerous experimental findings, the DMCS ligand therefore undergoes deviations of $\alpha$ and $\beta$ from 109.5 and 180°, respectively, in order to meet the structural requirements for the formation of isomer I or II (cf. Figs. 2b and 2c).

## Structural model considerations

Table 1 shows results of a simple model calculation of the variation of $d(M \cdots M')$ with changes in $\alpha$ and $\beta$ with a fixed value of $d$(M–Cent) of 2.50 Å. Interestingly, an increase or decrease of $\alpha$ by 10 degrees (from 109.5°) without any concomitant deviation of $\beta$ from 180° is insufficient for formation of either isomer.

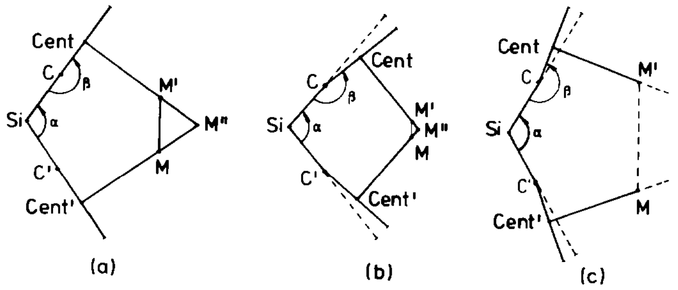

Fig. 2. Schematic view of the M–M′–Cent–C(ring)–Si–C(ring)′–Cent′ heptagon of isomer I ((b) $\alpha < 109.5°$, $\beta < 180°$) and isomer II ((c) $\alpha > 109.5°$, $\beta > 180°$). (a) idealized configuration ($\alpha = 109.5°$, $\beta = 180°$) with reasonable M–Cent separation, but too long $M^{II}$–Cent and too short M–M′ distance, respectively, to satisfy either of the two isomers.

Table 1

Variation of the separation $d(M \cdots M')$ of Fig. 2 with changes in the angles (°) $\alpha$ and $\beta$. $d$(M–Cent) = 2.50 Å

| $\alpha$ | $\beta$ | d(M···M') | Remarks | |
|---|---|---|---|---|
| 110 | 180 | 2.19 | unfavourable for isomer I and II | |
| 100 | 180 | 1.51 | | |
| 100 | 175 | 0.84 | tolerable for isomer I only in case of additional distortions | |
| 100 | 170 | 0.23 | | |
| 120 | 180 | 2.85 | tolerable for isomer II with | (X = H, Me) |
| 130 | 180 | 3.48 | | |
| 120 | 185 | 3.83 | | (X = halide) |
| 120 | 190 | 4.74 | | |

While only a concerted *widening* of $\alpha$ to about 120° and of $\beta$ to 185–190° would lead to the appropriate $M \cdots M'$ separations for numerous type II dimers, larger distortions would be required even after a corresponding *shrinkage* of $\alpha$ to 100°, and of $\beta$ to 175–170° to arrive at acceptable M–Cent values for isomer I. Thus, in the mononuclear (DMCS)$MCl_2$ systems (M = Ti and Zr), where the DMCS ligand has no alternative to chelating coordination, the values of $\alpha$ and $\beta$ are reduced to 89.5 and 160.9° for M = Ti, and to 93.2 and 165.8° for M = Zr, respectively [2]. For the related mononuclear complex $(C_6H_5)_2Si(\eta^6\text{-}C_6H_5)_2Cr^0$ the corresponding angles are 96.0 and 138° [3].

Table 2 shows that with $\alpha = 120°$ and $\beta = 190°$ the distance $d(M \cdots M')$ in isomer II is expected to increase moderately as the distance M–Cent decreases. On the other hand, for the members of any isostructural series $[(C_5H_5)_2M(\mu\text{-}X)]_2$ (with constant X, but M of variable size) the distance $M \cdots M'$ should decrease with decrease in the ionic radius of the metal ion and, hence, also with the distance M–Cent. Consequently, for constant values of $\alpha$ and $\beta$ [4*], and gradually increasing $r(M^{3+})$, the respective distances $d(M \cdots M')$ in the two isomers would rapidly diverge towards some "critical values" of $r(M^{3+})$ and M–Cent, respectively: For M–Cent values exceeding this "critical distance", isomer I would have become energetically more favourable than isomer II in that then the total amount of energy required to make the DMCS ligands chelating would even be lower than the energy

Table 2

Variation of the $M \cdots M$ separation with changes in the distance M–Cent. All distances in Å; $\alpha = 120$, $\beta = 190°$

| M–Cent | M···M | Remarks |
|---|---|---|
| 2.20 | 4.00 | M ≈ Sc |
| 2.30 | 3.95 | |
| 2.35 | 3.92 | M ≈ Yb |
| 2.40 | 3.88 | |
| 2.45 | 3.86 | M ≈ Pr |
| 2.50 | 3.83 | |

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* A reference number with an asterisk indicates a note in the list of references.

Table 3

Some significant structural data for the compounds **1**, **1a**, **1a′**, **4** and **4a**

| Compound | | Ref. | Yb···Yb′ (Å) | Yb–X [b] (Å) | Yb–X–Yb′ [b] (°) | α [c] (°) | β [d] (°) |
|---|---|---|---|---|---|---|---|
| $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$ | **1a** | [6] | 3.9875(7) | 2.639(3)–2.645(3) | 98.0(1) | – | – |
| | **1a′** [a] | – | 3.996(1)/4.019(2) | 2.633(5)–2.669(5) | 97.5(2)–99.7(2) | – | – |
| $[Me_2Si(C_5H_4)_2Yb(\mu\text{-}Cl)]_2$ | **1** | [5] | 3.750(2) | 2.636(1) | 90.8(3) | 118.7 | 186±0.5 |
| $[(C_5H_5)_2(Yb(\mu\text{-}Br)]_2$ | **4a** | [6] | 4.164(1)/4.187(1) | 2.786(3)–2.821(3) | 94.45(8)–97.27(8) | – | – |
| | | [8] | 4.1393(7) | 2.790(1)–2.800(1) | 95.22(4) | – | – |
| $[Me_2Si(C_5H_4)_2Yb(\mu\text{-}Br)]_2$ | **4** [a] | – | 3.797(1) | 2.760(1) | 86.9(1) | 118.9(4) | 187.3 |

[a] This paper. [b] X = halide atom. [c] C(ring)–Si–C(ring′). [d] Cent–C(ring)–Si.

necessary to give the $[M(\mu\text{-}X)\}_2$ fragment the unusually short $d(M \cdots M')$ value of isomer II.

A recent crystallographic X-ray study of $[(DMCS)Yb(\mu\text{-}Cl)]_2$ (**1**) [5] and a detailed mass spectrometric investigation [1] have confirmed that isomer II of **1** is strongly preferred. Interestingly, in crystalline **1** both $\alpha$ and $\beta$ deviate only moderately from 109.5 and 180° (Table 3), since $d(Yb \cdots Yb')$ turns out to be significantly shorter than in the dimer $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$, **1a/a′** [6]. Apparently, it would require substantially more energy to widen the angles $\alpha$ and $\beta$ of the coordinated DMCS ligands further than to deform the angles of the $\{Yb(\mu\text{-}Cl)\}_2$ skeleton of **1a/a′** so as to move the value of $d(Yb \cdots Yb')$ towards that in **1** (cf. Table 3). On the other hand, the mass spectrometric properties of the yttrium and yttrium/ytterbium analogues of **1**, $[(DMCS)Y(\mu\text{-}Cl)]_2$ (**2**) and $[(DMCS)Y(\mu\text{-}Cl)_2Yb(DMCS)]$ (**3**), respectively [1], differ significantly from those of **1**, suggesting that, at least for molecules of **2** and **3** in the vapour state, the "critical M–Cent distance" (*vide supra*) may have been reached [9]. While we have so far been unable to obtain crystals of **2** and **3** suitable for X-ray studies, we have been able to determine both the complete mass spectrum [7] and the low-temperature crystal structure for the new bromide analogue of **1**, $[(DMCS)Yb(\mu\text{-}Br)]_2$ (**4**).

## Structure of $[Me_2Si(C_5H_4)_2Yb(\mu\text{-}Br)]_2$, 4

As expected, the $Yb \cdots Yb'$ distance in the "parent" system of **4**, $[(C_5H_5)_2Yb(\mu\text{-}Br)]_2$ (**4a**) [6,8], exceeds clearly that in **1** (Table 3), and (by ca. 0.3 Å) also the value of $(Yb \cdots Yb)')$ estimated for isomer II of **4** (for $\alpha = 120°$ and $\beta = 185°$; see Table 1). Evenso, complex **4** turns out, again in good accordance with the mass spectroscopic data [7], to be fully isostructural with its chloride congener **1** (Figs. 3 and 4). The probably most conspicuous feature of its structure is the large reduction of the $Yb \cdots Yb'$ distance from ca. 4.16 Å in **4a** [8] to 3.797 Å*n* **4**. However, all the geometrical parameters for the $\{Yb(\mu\text{-}Br)\}_2$ fragments of **4** and **4a** differ only weakly. The complexes **1** and **4** also have in common that neither of their "best planes" Yb–X–Yb′–X′ and Si–X–Si′–X′ (X = halide) actually functions as a mirror plane of the molecule (Fig. 4). Thus the Si–Br1 distance is 3.910 Å and Si–Br2 is 4.21 Å; the absence of these mirror planes also favours a lengthening of $d(Yb \cdots Yb')$ [15].

The actual structure of **4** suggests that the $\{Yb(\mu\text{-}Br)\}_2$ skeleton is more readily deformable than that of its $\{Yb(\mu\text{-}Cl)\}_2$ counterpart and, in a sense, also more flexible than the $\{Yb(DMCS)\}_2$ fragment. The structure adopted is likely to result from an energetically optimally concerted distortion of both fragments which leaves available some potential for further widening of $\alpha$ and $\beta$. Formation of isomer II is thus conceivable even in the case of related $[(DMCS)Ln(\mu\text{-}X)]_2$ systems with $Ln^{3+}$ ions larger than $Yb^{3+}$ and/or bridging ligands X as large as, or slightly larger than, Br. For e.g. X = I, the $\{Yb(\mu\text{-}I)\}_2$ fragment would have to undergo much greater deformations both of its angles and of the Yb–I distances than for X = Br. Yet very recently a $\{Cr_2^{II}(\mu\text{-}I)_3\}$ fragment with Cr–I–Cr angles as acute as 67.8° (due to weak metal–metal bonding) has been described [10a] ($d$(Yb–I): ca. 3.0 Å [10b]). On the other hand, dimers involving bridging elements X less bulky than e.g. Cl should afford $\{Yb(\mu\text{-}X)\}_2$ fragments with $Yb \cdots Yb'$ separations fulfilling the requirements for the formation of isomer II. Some examples of structurally characterized

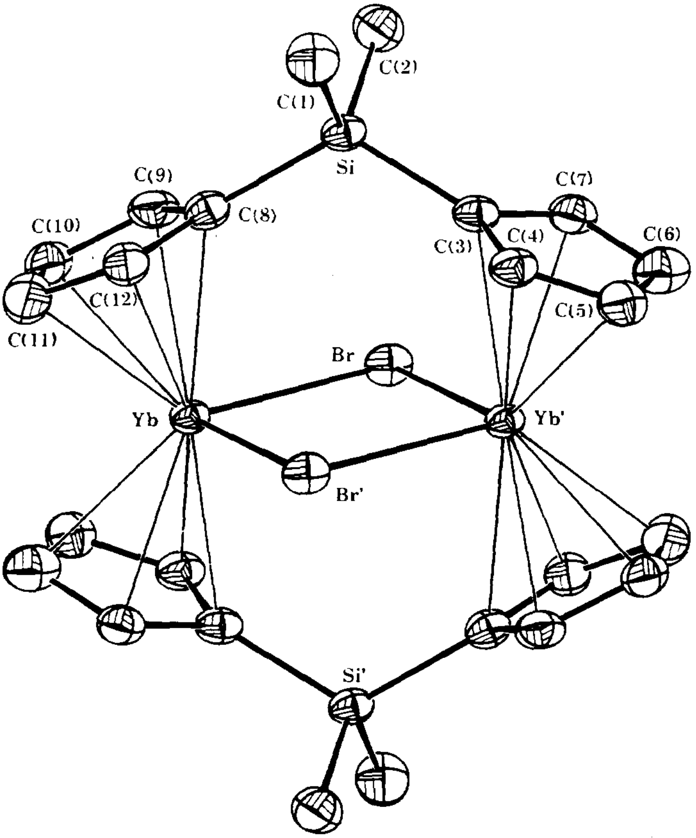

Fig. 3. ORTEP plot of $[Me_2Si(C_5H_4)_2Yb(\mu\text{-}Br)]_2$ (**4**); view along the plane of the $[Yb(\mu\text{-}Br)]_2$ skeleton.

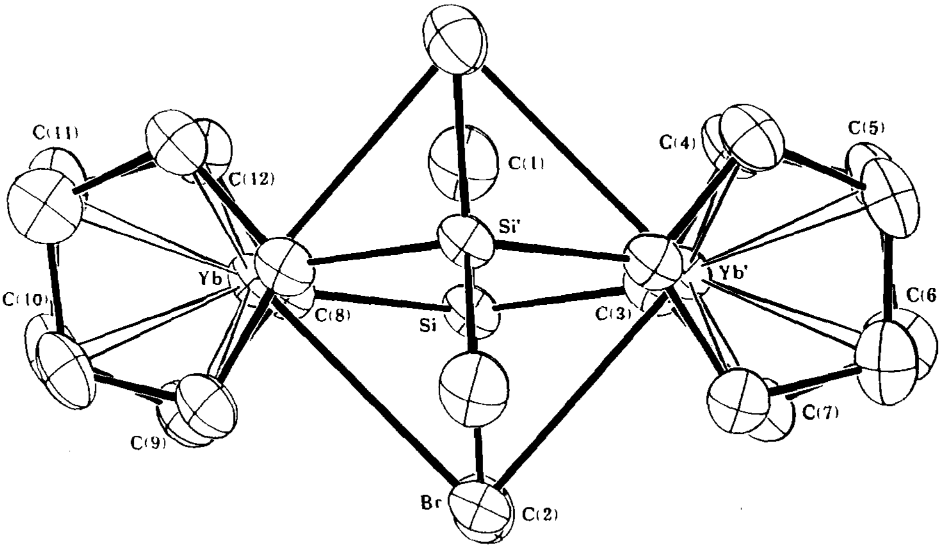

Fig. 4. ORTEP plot of $[Me_2Si(C_5H_4)_2Yb(\mu\text{-}Br)]_2$ (**4**); view perpendicular to the plane of the $[Yb(\mu\text{-}Br)]_2$ skeleton.

Table 4

Positional parameters of [$Me_2Si(C_5H_4)_2Yb(\mu$-Br)] (**4**) with esd's in parentheses and equivalent isotropic thermal parameters ($Å^2$)

| Atom | *x* | *y* | *z* | $B_{eq}$ |
|---|---|---|---|---|
| Yb | 0.33009(2) | 0.33824(5) | 0.47614(2) | 1.56 |
| Br | 0.24925(5) | 0.43465(11) | 0.58161(6) | 1.87 |
| Si | 0.13912(13) | 0.49332(31) | 0.33121(16) | 1.72 |
| C(1) | 0.0976(6) | 0.4589(15) | 0.2098(6) | 2.97 |
| C(2) | 0.1154(5) | 0.6952(12) | 0.3644(7) | 2.70 |
| C(3) | 0.1006(5) | 0.3435(12) | 0.3915(6) | 1.80 |
| C(4) | 0.0780(5) | 0.1832(12) | 0.3664(6) | 2.24 |
| C(5) | 0.0430(5) | 0.1224(13) | 0.4230(7) | 3.18 |
| C(6) | 0.0394(6) | 0.2432(14) | 0.4853(7) | 3.07 |
| C(7) | 0.0735(5) | 0.3788(12) | 0.4653(6) | 2.23 |
| C(8) | 0.2371(5) | 0.4928(11) | 0.3505(6) | 1.90 |
| C(9) | 0.2865(5) | 0.6096(12) | 0.4002(7) | 2.44 |
| C(10) | 0.3520(5) | 0.5830(13) | 0.3902(7) | 3.39 |
| C(11) | 0.3474(6) | 0.4510(15) | 0.3322(7) | 3.62 |
| C(12) | 0.2755(5) | 0.3961(13) | 0.3071(6) | 2.23 |

binuclear complexes with M–M′ separations shorter than $d$(Yb $\cdots$ Yb′) in **1** are presented in Table 6. In the related cyclic complexes $\mu$-{$Me_2Si(C_5H_4)_2$}($\mu$-$CO)_2Fe_2(CO)_2$ with $d$(Fe $\cdots$ Fe) = 2.51 Å the angle $\alpha$ even turns out to be less than 109.5° [18].

When a group R bulkier than a hydrogen atom is bonded to all the ring carbon atoms most remote from the silylated ones the formation of isomer II may be hampered by a different obstacle. Apparently these eight ring substituents R (i.e. two on each ring) would adopt spatially close-lying and pairwise strictly eclipsed

Table 5

Selected intramolecular distances (Å) and angles (°) of [$Me_2Si(C_5H_4)_2Yb(\mu$-Br)$]_2$ (**4**)

| | | | |
|---|---|---|---|
| Yb–Yb′ | 3.797(1) | C(3)–C(4) | 1.426(13) |
| Yb–Br | 2.760(1) | C(3)–C(7) | 1.451(13) |
| Yb–C(8) | 2.603(9) | C(4)–C(5) | 1.382(14) |
| Yb–C(9) | 2.580(9) | C(5)–C(6) | 1.421(16) |
| Yb–C(10) | 2.554(9) | C(6)–C(7) | 1.402(15) |
| Yb–C(11) | 2.566(10) | C(8)–C(9) | 1.436(13) |
| Yb–C(12) | 2.590(9) | C(8)–C(12) | 1.419(13) |
| Si–C(1) | 1.857(10) | C(9)–C(10) | 1.384(14) |
| Si–C(2) | 1.863(11) | C(10)–C(11) | 1.412(17) |
| Si–C(3) | 1.867(10) | C(11)–C(12) | 1.444(14) |
| Si–C(8) | 1.888(10) | | |
| Yb–Br–Yb′ | 86.9(1) | C(3)–Si–C(8) | 118.9(4) |
| Br–Yb–Br′ | 93.1(1) | C(4)–C(3)–C(7) | 104.3(8) |
| C(1)–Si–C(2) | 110.7(5) | C(3)–C(4)–C(5) | 110.2(9) |
| C(1)–Si–C(3) | 107.1(5) | C(4)–C(5)–C(6) | 109.0(9) |
| C(1)–Si–C(8) | 106.4(4) | C(5)–C(6)–C(7) | 106.6(9) |
| C(2)–Si–C(3) | 106.4(4) | C(3)–C(7)–C(6) | 109.9(9) |
| C(2)–Si–C(8) | 107.3(4) | Yb–C(8)–Si | 126.1(4) |

Table 6

Some M···M distances (Å) shorter than 3.90 Å in binuclear complexes containing a $\{M(\mu\text{-}X)\}_2$ fragment

| Complex | $d(M\cdots M)$ (Å) | Ref. |
|---|---|---|
| $[(C_5H_5)_2Sc(\mu\text{-}Cl)]_2$ | 3.886 | 11 |
| $[(Me_3CC_5H_4)_2Ce(\mu\text{-}OCHMe_2)]_2$ | 3.844 | 22 |
| $[(MeC_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ | 3.667 | 12 |
| $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$ | 3.599 | 13, 14 |
| $[(C_5H_5)_2Yb(\mu\text{-}Me)]_2$ | 3.484 | 14 |
| $[(C_5H_5)_2Lu(\mu\text{-}O(CH_2)_4PPh_2)]_2$ | 3.476 | 16 |
| $[Et_2Si(C_5H_4)(C_5Me_4)Lu(\mu\text{-}H)]_2$ | 3.390 | 17 |

positions, an arrangement which might energetically less favourable than that in isomer I. A simple model calculation suggests that steric hindrance should become significant for Cent–M–Cent′ angles < 115° (R = H) and < 125° (R = Me), respectively (**4**: Cent–Yb–Cent′ = 132.7°). Interestingly, the dimers $[Me_2Si(C_5Me_4)_2Ln(\mu\text{-}H)]_2$ with Ln = Nd, Sm and Lu [19] seem to prefer the structure of isomer I, although the "critical Ln–Cent values" (*vide supra*) may not have been reached. On the other hand, the complex $[Et_2Si(C_5H_4)(C_5Me_4)Lu(\mu\text{-}H)]_2$ (Table 6) has been shown [17*] to adopt the centrosymmetrical configuration of isomer II in which pairs of mutually eclipsed methyl groups are avoided.

Currently, complexes of tetra- or trivalent metal ions involving two unsymmetrically modified cyclopentadienyl ligands interlinked by a $SiR_2$ or $C_2R_4$ bridge are being increasingly studied as a potential pool of stereo- or even enantio-selective catalysts [20,23] for olefin hydrogenation or polymerization. Since mainly dimers of type I would have a chance of co-existing in equilibrium with the coordinatively unsaturated monomers (the potential catalyst precursors), maximum understanding of all the factors affecting the predominance of isomer I is important.

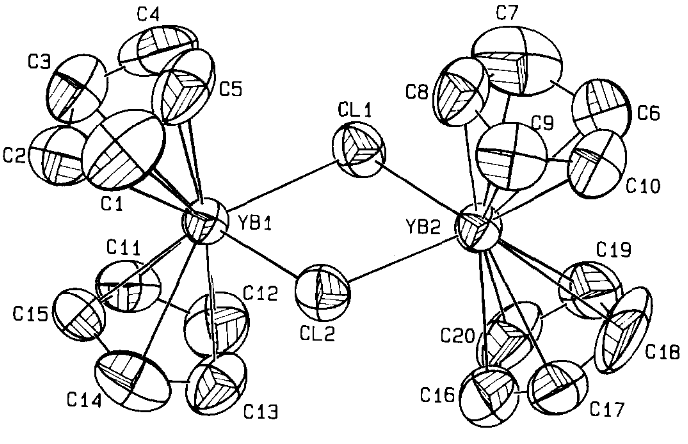

Fig. 5. ORTEP plot of one of the two practically equal $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$ molecules of species **1a′**.

## Structure of non-sublimed $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$, 1a′

It was observed fortuitously that needle-shaped red crystals grew from a green solution of a 3 : 1 mixture of $(C_5H_5)_3Yb$ and $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$ (**1a**) in n-hexane. The single crystal X-ray study of a selected crystal revealed that from this particular solution only complex **1a** had crystallized, albeit in a modification different from that obtained by controlled sublimation [6]. Since the molecular structure of **1a′** is of some relevance for the preceding discussion, we present briefly below the results of an X-ray diffraction study of **1a′** crystallized from solution.

Although **1a** (sublimed) and **1a′** (from solution) crystallize in the same space group, their lattice parameters and $Z$-values are different. Table 7 present crystal data and details of the data collection and refinement for **1a′** and **4**. As the cell parameters for **1a′** resembled those of compound **4a** [6], the structure of the latter served as a starting model for subsequent refinements. Hence, the packing of the binuclear molecules in **1a′** corresponds to that in the previously studied crystals of **4a** and $[(C_5H_5)_2Sc(\mu\text{-}Cl)]_2$, in which two molecules occupy crystallographically non-equivalent positions [11]. In contrast, **1a** is isostructural with $[(C_5H_5)_2Er(\mu\text{-}Cl)]_2$ obtained by sublimation [21] and the crystal contains only one type of dimer. The atomic parameters for **1a′** are given in Table 8, and selected bond distances and

Table 7

Summary of crystal data and details of data collection and refinement for **1a′** and **4**

| | $[Me_2Si(C_5H_4)_2Yb(\mu\text{-}Br)]_2$ (**4**) | $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$ (**1a′**) |
|---|---|---|
| Crystal size (mm) | 0.15×0.20×0.20 | 0.15×0.30×0.35 |
| Crystal system | monoclinic | monoclinic |
| Space group | $C2/c$ (No. 15) | $P2_1/c$ (No. 14) |
| $a$ (Å) | 19.981(28) | 13.634(3) |
| $b$ (Å) | 8.325(11) | 16.251(3) |
| $c$ (Å) | 15.703(8) | 13.659(3) |
| $\beta$ (°) | 107.7(1) | 92.65(2) |
| $V$ (Å$^3$) | 2489.00 | 3023.14 |
| $Z$ (dimers) | 4 | 6 |
| $D_c$ (gcm$^{-3}$) | 2.344 | 2.232 |
| $F$(000) | 1640 | 1884 |
| Diffractometer | Enraf–Nonius CAD-4 | Syntex $P2_1$ |
| Temperature (K) | 140±5 | 293 |
| Radiation λ (Å) [a] | 0.71069 | 0.71069 |
| $\mu$(Mo-$K_\alpha$) (cm$^{-1}$) | 104.0 | 90.81 |
| Scan technique | $\omega-2\theta$ scan | $\omega$-scan |
| $2\theta$ Range | $1 \leqslant 2\theta \leqslant 55$ | $1 \leqslant 2\theta \leqslant 50$ |
| No. reflections | 6470 | 5874 |
| No. unique reflections | 2537 | 4724 |
| No. reflections in refinement | 2254 [b] | 3854 |
| No. refined parameters | 136 | 327 |
| Largest peak in final difference Fourier syntheses (e Å$^{-3}$) | 1.45 | 1.52 |
| Absorption correction | $T_{min}$ 48.8%; $T_{max}$ 99.8% | DIFABS |
| $R$ | 0.031 [c] | 0.055 |

[a] Graphite monochromator. [b] $F_o \geqslant 4\sigma(F_o)$. [c] Final $R = \Sigma\| F_o | - | F_o \|/\Sigma| F_o |$.

Table 8

Positional parameters of $[(C_5H_5)_2Yb(\mu\text{-Cl})]$ (1a′) with esd's in parentheses and equivalent isotropic thermal parameters (Å$^2$)

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Yb1 | 0.2450(1) | 0.1028(1) | 0.0563(1) | 3.82 |
| Yb2 | 0.4443(1) | 0.2653(1) | 0.1586(1) | 3.86 |
| Yb3 | 0.9123(1) | 0.0873(1) | 0.4392(1) | 3.74 |
| Cl1 | 0.2888(4) | 0.1846(3) | 0.2205(3) | 4.70 |
| Cl2 | 0.4037(4) | 0.1769(3) | −0.0028(4) | 5.08 |
| Cl3 | 0.0813(3) | 0.4258(3) | 0.0394(4) | 4.82 |
| C1 | 0.3356(27) | −0.0320(19) | 0.0134(32) | 9.92 |
| C2 | 0.2479(29) | −0.0489(15) | 0.0057(20) | 7.64 |
| C3 | 0.2012(18) | −0.0501(14) | 0.1044(22) | 6.50 |
| C4 | 0.2769(34) | −0.0258(15) | 0.1642(20) | 9.85 |
| C5 | 0.3554(21) | −0.0165(16) | 0.1083(33) | 8.86 |
| C6 | 0.5804(17) | 0.2683(16) | 0.2934(18) | 5.46 |
| C7 | 0.5378(17) | 0.1889(23) | 0.2974(25) | 12.35 |
| C8 | 0.5602(16) | 0.1473(15) | 0.2124(22) | 6.68 |
| C9 | 0.6174(16) | 0.1986(16) | 0.1623(19) | 6.71 |
| C10 | 0.6261(14) | 0.2717(13) | 0.2171(19) | 5.92 |
| C11 | 0.0613(17) | 0.1331(15) | 0.0305(17) | 6.94 |
| C12 | 0.1059(20) | 0.2098(15) | 0.0392(22) | 7.11 |
| C13 | 0.1564(17) | 0.2180(15) | −0.0422(22) | 7.08 |
| C14 | 0.1440(17) | 0.1504(19) | −0.9083(18) | 7.47 |
| C15 | 0.0868(17) | 0.0954(14) | −0.0476(14) | 5.21 |
| C16 | 0.3599(23) | 0.3813(14) | 0.0518(23) | 7.79 |
| C17 | 0.4543(21) | 0.4020(14) | 0.0643(18) | 6.74 |
| C18 | 0.4866(24) | 0.4198(13) | 0.1533(32) | 11.97 |
| C19 | 0.3925(25) | 0.4079(15) | 0.2143(17) | 6.72 |
| C20 | 0.3244(20) | 0.3847(14) | 0.1427(27) | 8.36 |
| C21 | 0.1177(31) | 0.5673(18) | 0.2466(15) | 9.59 |
| C22 | 0.0203(23) | 0.5513(27) | 0.2239(18) | 8.07 |
| C23 | −0.0255(24) | 0.6186(29) | 0.1996(17) | 8.45 |
| C24 | 0.0363(32) | 0.6817(21) | 0.1974(22) | 8.45 |
| C25 | 0.1298(20) | 0.6504(25) | 0.2323(18) | 7.70 |
| C26 | 0.1513(24) | 0.6373(34) | −0.1010(24) | 14.23 |
| C27 | 0.1636(22) | 0.7015(17) | −0.0411(27) | 7.35 |
| C28 | 0.2325(31) | 0.6792(28) | 0.0246(23) | 10.43 |
| C29 | 0.2577(21) | 0.5977(29) | −0.0012(31) | 13.83 |
| C30 | 0.2096(36) | 0.5767(24) | −0.0768(30) | 10.54 |

bond angles in Tables 9 and 10. The corresponding intramolecular distances and angles for **1a** and **1a′** do not differ significantly, but it should be noted that only complex **1a** has been found to be able to crystallize like *both* its Sc and its Er analogue.

## Experimental

The burgundy-coloured new compound **4** (m.p.: 157 °C) was prepared from anhydrous $YbBr_3$ and $Na_2[Me_2Si(C_5H_4)_2]$ by the procedure described in Ref. 1 (yield ca. 90%). Single crystals were grown from a concentrated solution in toluene

Table 9

Interatomic distances (Å) of $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$ (**1a′**) with esd's in parentheses [a,b]

| | | | |
|---|---|---|---|
| Yb1–Yb2 | 3.996(1) | Yb3–Yb3* | 4.019(2) |
| Cl1–Cl2 | 3.495(9) | Cl3–Cl3* | 3.417(9) |
| Yb1–Cl1 | 2.651(5) | Yb1–Cl2 | 2.635(5) |
| Yb2–Cl1 | 2.664(5) | Yb2–Cl2 | 2.669(5) |
| Yb3–Cl3 | 2.642(5) | Yb3–Cl3* | 2.633(5) |
| *Next but one metal–metal distances* | | | |
| Yb1–Yb1 | 7.563(1) | Yb1–Yb2 | 6.546(1) |
| Yb2–Yb2 | 6.848(1) | Yb2–Yb3 | 7.225(1) |
| Yb3–Yb3 | 8.638(1) | Yb3–Yb1 | 6.916(1) |
| Yb1–C1 | 2.595(34) | Yb1–C11 | 2.562(23) |
| Yb1–C2 | 2.561(24) | Yb1–C12 | 2.575(26) |
| Yb1–C3 | 2.646(24) | Yb1–C13 | 2.574(25) |
| Yb1–C4 | 2.583(26) | Yb1–C14 | 2.586(25) |
| Yb1–C5 | 2.535(28) | Yb1–C15 | 2.529(21) |
| Yb1–Z1 | 2.312(40) | Yb1–Z3 | 2.293(40) |
| Yb2–C6 | 2.553(23) | Yb2–C16 | 2.617(27) |
| Yb2–C7 | 2.557(33) | Yb2–C17 | 2.574(23) |
| Yb2–C8 | 2.570(23) | Yb2–C18 | 2.577(22) |
| Yb2–C9 | 2.595(22) | Yb2–C19 | 2.550(25) |
| Yb2–C10 | 2.570(20) | Yb2–C20 | 2.540(25) |
| Yb2–Z4 | 2.285(40) | Yb2–Z2 | 2.293(40) |
| Yb3–C21 | 2.573(32) | Yb3–C26 | 2.544(28) |
| Yb3–C22 | 2.518(25) | Yb3–C27 | 2.567(26) |
| Yb3–C23 | 2.551(31) | Yb3–C28 | 2.543(32) |
| Yb3–C24 | 2.540(23) | Yb3–C29 | 2.510(35) |
| Yb3–C25 | 2.598(32) | Yb3–C30 | 2.572(23) |
| Yb3–Z5 | 2.279(30) | Yb3–Z6 | 2.273(40) |
| C1–C2 | 1.226(53) | C6–C7 | 1.418(44) |
| C1–C5 | 1.336(61) | C6–C10 | 1.239(35) |
| C2–C3 | 1.518(43) | C7–C8 | 1.389(45) |
| C3–C4 | 1.346(46) | C8–C9 | 1.350(35) |
| C4–C5 | 1.351(55) | C9–C10 | 1.407(34) |
| C11–C12 | 1.389(35) | C16–C17 | 1.333(42) |
| C11–C15 | 1.292(31) | C16–C20 | 1.354(49) |
| C12–C13 | 1.341(41) | C17–C18 | 1.307(49) |
| C13–C14 | 1.345(39) | C18–C19 | 1.575(49) |
| C14–C15 | 1.392(35) | C19–C20 | 1.371(42) |
| C21–C22 | 1.374(52) | C26–C27 | 1.331(58) |
| C21–C25 | 1.375(49) | C26–C30 | 1.298(64) |
| C22–C23 | 1.296(58) | C27–C28 | 1.319(50) |
| C23–C24 | 1.328(57) | C28–C29 | 1.417(64) |
| C24–C25 | 1.434(50) | C29–C30 | 1.244(57) |

[a] Asterisk denotes a symmetry related position. Z: the centroid of the cyclopentadienyl ring. [b] The atoms Yb1, Yb2, Cl1, Cl2 and C1–C20 belong to molecule 1, all other atoms to molecule 2 (cf. Fig. 5).

(temperature: ca. 5 ° C, duration: ca. 3 days). The IR and the NIR/VIS spectra of **4** are practially superimposable on those of complex **1**.

The selected crystal mounted on a glass fibre, was exposed to a continuous stream of cold $N_2$ (140 ± 5 K) within the diffractometer. Accurate cell dimensions

Table 10

Selected bond angles (°) of $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$ (**1a′**) with esd's in parentheses

| | | | |
|---|---|---|---|
| Cl2–Yb1–Cl1 | 82.8(2) | Yb2–Cl1–Yb1 | 97.5(2) |
| Cl2–Yb2–Cl1 | 81.9(2) | Yb2–Cl2–Yb1 | 97.8(2) |
| Cl3–Yb3–Cl3* | 80.7(2) | Yb3–Cl3–Yb3* | 99.7(2) |
| Z1–Yb1–Z3 | 129.5(16) | Z2–Yb2–Z4 | 128.4(15) |
| Z5–Yb3–Z6 | 132.3(15) | | |
| C5–C1–C2 | 106.1(35) | C10–C6–C7 | 107.2(24) |
| C3–C2–C1 | 112.0(30) | C8–C7–C6 | 107.8(26) |
| C4–C3–C2 | 101.2(26) | C9–C8–C7 | 106.1(24) |
| C5–C4–C3 | 107.2(28) | C10–C9–C8 | 106.8(23) |
| C4–C5–C1 | 113.4(31) | C9–C10–C6 | 112.1(22) |
| C15–C11–C12 | 111.3(23) | C20–C16–C17 | 104.9(26) |
| C13–C12–C11 | 105.0(23) | C18–C17–C16 | 117.2(29) |
| C14–C13–C12 | 119.5(23) | C19–C18–C17 | 102.5(25) |
| C15–C14–C13 | 107.5(22) | C20–C19–C18 | 101.4(25) |
| C14–C15–C11 | 106.5(22) | C19–C20–C16 | 114.0(27) |
| C22–C21–C25 | 105.9(31) | C27–C26–C30 | 112.3(32) |
| C21–C22–C23 | 110.3(35) | C26–C27–C28 | 105.6(32) |
| C22–C23–C24 | 111.0(33) | C27–C28–C29 | 105.1(32) |
| C23–C24–C25 | 105.9(32) | C28–C29–C30 | 109.7(36) |
| C21–C25–C24 | 106.6(30) | C26–C30–C29 | 107.3(40) |

[a] Asterisk denotes a symmetry related position. Z: The centroid of the cyclopentadienyl ring.

and the crystal orientation matrix were determined by a least-squares treatment of the setting angles of 25 reflections in the range $14 \leqslant 2\theta \leqslant 24°$. The intensities of three selected reflections were monitored every 1.5 h for crystal decay, and during the data collection (total exposure: 71.1 h) there was a maximum fluctuation of 2.1%. The crystal orientation was checked at intervals of 20 intensity measurements by scanning three reflections distributed in reciprocal space. For angular changes $> 0.1°$ a new orientation matrix was calculated automatically from a list of 25 recentred reflections.

Systematic absence characteristic of the space group *Cc* and *C*2/*c* ($hkl$, $h + k\nu 2n$ and $h0l$, $l \neq 2n$) were subsequently identified from the full data set. The structure was solved in the space group *C*2/*c*. Data were corrected for polarization and Lorentz effects. An empirical absorption correction was based on a series of $\psi$ scans using the SDP [24]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations using SHELX-76 [25]. H atoms were included in the refinement at calculated positions (C–H: 1.08 Å) with a fixed isotropic thermal parameter ($U_{\text{iso,H}} = 0.08$ Å$^2$).

A single crystal of **1a′** was placed in a glass capillary. Unit-cell parameters were determined from 25 reflections ($5 \leqslant 2\theta \leqslant 25°$) and refined by the least-squares procedure. Two standard reflections were monitored every 100 reflections. 5874 reflections were collected (range of *h*, *k*, *l*: 0 to 16, 0 to 19, −16 to 16). The data were corrected for Lorentz and Polarisation effects and equivalent reflections averaged. Absorption correction was applied by the empirical method (DIFABS) [26]. The coordinates of the ytterbium atoms were obtained from Patterson syntheses [27]. The coordinates of all other non-hydrogen atoms were obtained after successive difference Fourier syntheses, and in the final cycles of full-matrix least-squares refinement all non-hydrogen atoms were treated anisotropically, with the hydrogen atoms included in calculated positions (C–H: 0.95 Å) with common isotropic temperature factors (SHELX-76) [25]. The atomic scattering factors $f_0$ and anomalous dispersion terms $f'$, $f''$ were taken from Ref. 28.

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*Note added in proof* (after the appearance of ref. 17b): The clean course of the facile hydrogenation reaction:

$$2Et_2Si(C_5Me_4)(C_5H_4)LuCH(SiMe_3)_2 \xrightarrow[\text{(pentane)}]{H_2} 5\ (\text{type II dimer}) + 2CH_2(SiMe_3)_2$$

reported in ref. 17b may serve as another experimental confirmation of the conclusion outlined in the present paper.

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