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FULL PAPER

Variability of (ring centroid)–Ln–(ring centroid) angles in the mixed ligand C_5Me_5/C_8H_8 complexes $(C_5Me_5)Ln(C_8H_8)$ and $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$

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The trivalent mixed ligand metallocene complexes $(C_5Me_5)Ln(C_8H_8)$ have been structurally characterized for Ln = Sm, Dy, Er, and Yb and compared with the known lutetium analog to study the effect of radial size and f^n electron configuration on the (C_5Me_5 ring centroid)–Ln–(C_8H_8 ring centroid) angles. Analogous angles were also examined in the mixed ligand, bimetallic, partially-solvated complex $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$.

Introduction

Since the discovery of the unusual bent structure of $(C_5Me_5)_2Sm$,[1,2] there has been considerable interest in the factors which affect (ring centroid)–Ln–(ring centroid) angles in unsolvated organometallic divalent lanthanide complexes.[3] The Eu[2] and Yb[4] analogs are also bent and several analogous alkaline earth complexes have also been structurally characterized.[5] Hanusa has correlated these data and shown that the larger the metal, the more bent is the structure.[6] This is similar to the structural trend in alkaline earth dihalides, MX_2, namely that bent structures are favored by the larger metals.[7] The overall problem is part of the general question of bent *versus* linear structures for ML_2 species.[8]

Recently, a new series of divalent lanthanide complexes in which the metal is sandwiched between two polyhapto anionic organic rings has been discovered which provides more experimental data on this question: the triple decked $[(C_5Me_5)Ln]_2(C_8H_8)$ complexes (Ln = Eu, Yb,[9] Sm[10]). It was not readily predictable if these complexes would have parallel ring planes or bent structures since the $(C_5Me_5)_2Ln$ compounds were all bent and bis(C_8H_8) f element complexes, $(C_8H_8)_2M$, were all linear, *i.e.* they had parallel ring planes.[11,12,13] The linear bis(cyclooctatetraenyl) complexes included not only a divalent lanthanide example, $[(C_8H_8)_2Yb]^{2-}$,[13] but also examples with metals in +3 and +4 oxidation states: $(C_8H_8)_2U$,[11] $[(C_8H_8)_2U]^-$[12] and $(C_8H_8)_2Ce$.[12] X-Ray diffraction studies revealed that the $[(C_5Me_5)Ln]_2(C_8H_8)$ complexes have bent structures, *i.e.* the geometry of the C_5Me_5 ligands prevailed over the geometry of the C_8H_8 groups in these divalent complexes.

The generality of the linear structures of the $(C_8H_8)_2M$ complexes regardless of oxidation state raised the question of how the bent structures of mixed ligand C_5Me_5/C_8H_8 complexes varied as a function of oxidation state. In addition to the divalent examples mentioned above, only a single example of a trivalent complex, $(C_5Me_5)Lu(C_8H_8)$, was available for comparison.[14] This single structure could not define a trend for the trivalent systems and more data were needed on complexes of this type. In addition, the observed 172.9° (ring centroid)–Ln–(ring centroid) angle of $(C_5Me_5)Lu(C_8H_8)$ could be rationalized to follow either trend. It could be considered to be nearly linear (a) because it followed the $M(C_8H_8)_2$ pattern or (b) because it followed the $(C_5Me_5)_2M$ structural trend where the small lutetium would favor only a slightly bent structure.

We report here the structures of four additional trivalent $(C_5Me_5)Ln(C_8H_8)$ complexes. The structure of the unusual mixed ligand C_5Me_5/C_8H_8 divalent complex, the *half-solvated* $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$, is also reported and provides additional data on the factors which affect bending in complexes of this type.

Experimental

All manipulations described below employing $(C_5Me_5)Ln(C_8H_8)$ and $[(C_5Me_5)Ln]_2(C_8H_8)$ were carried out under argon in an inert atmosphere glovebox free of coordinating solvents. All other chemistry was performed under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox techniques. Physical measurements were obtained and solvents were purified as previously described.[15] $(C_5Me_5)Sm(C_8H_8)$,[10] $(C_5Me_5)Dy(C_8H_8)$,[14] $(C_5Me_5)Er(C_8H_8)$,[14] and $(C_5Me_5)Yb(C_8H_8)$[9] were prepared as previously described.

Collection of X-ray diffraction data, solution and refinement for 1–4 and 6

All crystals were coated with Paratone oil, mounted on glass fibers and transferred to the Siemens CCD platform diffractometer under a cold stream. The SMART[16] program package was used to determine the unit-cell parameters and for data collection. The raw frame data were processed using SAINT[17] and SADABS[18] to yield the reflection data files. Subsequent calculations were carried out using the SHELXTL[19] program. In each case, the diffraction symmetry was *mmm* and the space group for **1**–**4** was *Pnma* while for **6** it was *Pbca*. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques and analytical scattering factors for neutral atoms were used throughout the analysis.[20] Hydrogen atoms were included using a riding model. Disorder in the cyclooctatetraene dianion rings of **2** and **4** and in the C_5Me_5 rings in **3** and **6** was modeled by assigning partial occupancy to the disordered components. No effect of the disorder on the (ring centroid)–metal–(ring centroid) angles was observed. Experimental parameters for the data collection and structure refinement of **1**–**4** and **6** are given in Table 1. Important bond distances and angles for **1**–**4** are given in Table 2 and for **6** in Table 3.

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See http://www.rsc.org/suppdata/dt/a9/a908412f/ for crystallographic files in .cif format.

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Table 1 Experimental data for $(C_5Me_5)Sm(C_8H_8)$, **1**, $(C_5Me_5)Dy(C_8H_8)$, **2**, $(C_5Me_5)Er(C_8H_8)$, **3**, $(C_5Me_5)Yb(C_8H_8)$, **4**, and $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$, **6**

Compound	1	2	3	4	6
Formula	$C_{18}H_{23}Sm$	$C_{18}H_{23}Dy$	$C_{18}H_{23}Er$	$C_{18}H_{23}Yb$	$C_{32}H_{46}OYb_2$
M	389.71	401.86	409.65	412.40	792.77
T/K	158	158	158	158	158
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pbca*
a/Å	10.4410(6)	10.3676(13)	10.3343(5)	10.3018(5)	16.7103(8)
b/Å	12.8707(8)	12.9050(16)	12.9440(6)	13.0166(6)	14.8166(7)
c/Å	11.7331(7)	11.6964(15)	11.6595(6)	11.6035(6)	25.1683(12)
$V/Å^3$	1576.7	1564.9	1559.66	1555.96	6231.4(5)
Z	4	4	4	4	8
$\rho_c/Mg\ m^{-3}$	1.642	1.706	1.745	1.760	1.690
μ/mm^{-1}	3.709	4.760	5.366	3.709	5.986
*R*1	0.0440	0.0362	0.0189	0.0237	0.0670
$wR2\ [I > 2\sigma(I)]$	0.0485	0.0967	0.0405	0.0616	0.0998

Table 2 Relevant bond lengths (Å) and angles (°) for $(C_5Me_5)Sm(C_8H_8)$, **1**, $(C_5Me_5)Dy(C_8H_8)$, **2**, $(C_5Me_5)Er(C_8H_8)$, **3**, $(C_5Me_5)Yb(C_8H_8)$, **4**, and $(C_5Me_5)Lu(C_8H_8)$, **5**

Complex	1	2	3	4	5
Ionic radius[a]	1.079	1.027	1.004	0.985	0.977
Ln–C(C_5Me_5) distance	2.668(3)	2.606(4)	2.579(2)	2.550(3)	2.537(1)
[Ln–C(C_5Me_5)]-ionic radius	1.589	1.579	1.575	1.565	1.560
Ln–Cnt(1)[b] distance	2.374	2.306	2.274	2.244	2.228(8)
[Ln–Cnt(1)]-ionic radius	1.295	1.279	1.270	1.259	1.251
Ln–C(C_8H_8) distance	2.558(6)	2.551(3)	2.523(4)	2.479(6)	2.433(3)
[Ln–C(C_8H_8)]-ionic radius	1.479	1.524	1.519	1.494	1.466
Ln–Cnt(2)[c] distance	1.838	1.759	1.725	1.654	1.634(7)
[Ln–Cnt(2)]-ionic radius	0.759	0.768	0.721	0.669	0.657
Cnt(1)–Ln–Cnt(2) angle	164.3	169.7	171.2	171.5	172.9

[a] Eight coordinate ionic radii from ref. 21. [b] Cnt(1) is the centroid of the pentamethylcyclopentadienide ring. [c] Cnt(2) is the centroid of the cyclooctatetraene dianion ring.

Results

$(C_5Me_5)Ln(C_8H_8)$ Complexes

The solid state structures of $(C_5Me_5)Sm(C_8H_8)$, **1**, $(C_5Me_5)Dy(C_8H_8)$, **2**, $(C_5Me_5)Er(C_8H_8)$, **3**, and $(C_5Me_5)Yb(C_8H_8)$, **4**, were determined for comparison with that of $(C_5Me_5)Lu(C_8H_8)$, **5**.[14] Attempts to obtain crystals suitable for X-ray crystallography for lanthanides larger than Sm were unsuccessful in our hands. These larger metals readily crystallize as solvates, *e.g.* $(C_5Me_5)Ln(C_8H_8)(THF)$[14] (Ln = La, Pr), rather than as unsolvated species. The structures of **1**–**4** are similar to that of **5** and a representative structure of $(C_5Me_5)Er(C_8H_8)$ is shown in Fig. 1. A summary of bond lengths and angles for these compounds is presented in Table 2.

The Ln–C(C_5Me_5) and Ln–C(C_8H_8) distances decrease from **1** to **5** with changes that follow the differences in eight-coordinate metal radii.[21] This is most easily seen by examining the similarity of the entries in the rows labelled [Ln–C(C_5Me_5)]-ionic radius, [Ln–Cnt(1)]-ionic radius, [Ln–C(C_8H_8)]-ionic radius and [Ln–Cnt(2)]-ionic radius. None of these numbers is unusual compared to previous data in the literature.[11c] These rows show that the average Ln–C(C_5Me_5) distances follow the trend in ionic radii closer than the average Ln–C(C_8H_8) distances.

The 164.3°, 169.7°, 171.2° and 171.5° (C_5Me_5 ring centroid)–Ln–(C_8H_8 ring centroid) angles for **1**–**4**, respectively, are smaller than the 172.9° angle of **5** and they follow the trend that the larger the metal, the more the structure is bent (smaller angle). These data are plotted in Fig. 2 and discussed below.

$[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$, 6

Complex **6** was fortuitously obtained from a reaction of one-half equivalent of Al_2Et_6 with one equivalent of $[(C_5Me_5)Yb(THF)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ in efforts to determine if a $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)(THF)\cdot AlEt_3]$ complex analogous to the complex, $(C_5Me_5)_2Yb\cdot AlEt_3(THF)$,[22] would form. Although evidence for the triethylaluminum adduct was obtained by ^1H NMR spectroscopy, recrystallization gave the asymmetric, half-solvated bimetallic $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$, **6**, Fig. 3, the structural data of which are reported here since they are relevant to bending in metallocene systems.

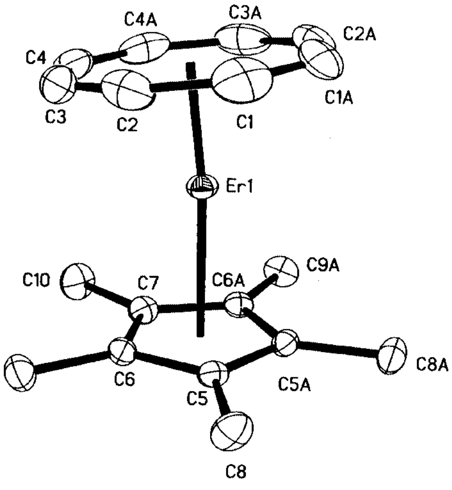

Fig. 1 Thermal ellipsoid plot of $(C_5Me_5)Er(C_8H_8)$, **3**, with ellipsoids drawn at the 50% probability level.

The bond lengths and angles in **6** are significantly different on the solvated and unsolvated sides of the complex and are compared to the data on unsolvated $[(C_5Me_5)Yb]_2(C_8H_8)$ **7**[9] and $[(C_5Me_5)Sm]_2(C_8H_8)$ **8**[10] and solvated $[(C_5Me_5)Sm(MeOCH_2CH_2OMe)]_2(C_8H_8)$ **9**[10] in Table 3. The Yb(1)–C(C_5Me_5) average distance is 2.683(3) Å on the solvated side *versus* 2.615(3) Å for

Table 3 Relevant bond lengths (Å) and angles (°) for $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$, **6**, $[(C_5Me_5)Yb]_2(C_8H_8)$, **7**, $[(C_5Me_5)Sm]_2(C_8H_8)$, **8**, and $[(C_5Me_5)Sm(MeOCH_2CH_2OMe)]_2(C_8H_8)$, **9**

	6	**7**	**8**	**9**
Ln(1)–Cnt(1)[a]	2.391	2.338	2.510	2.653
Ln(1)–Cnt(2)[b]	2.087	1.909	2.151	2.344
Ln(2)–Cnt(2)	1.881	1.926	2.120	2.344
Ln(2)–Cnt(3)[c]	2.320	2.346	2.497	2.653
Ln(1)–C(C_5Me_5)	2.683(3)	2.632(6)	2.79(1)	2.910(6)
Ln(2)–C(C_5Me_5)	2.615(3)	2.636(2)	2.77(1)	2.910(6)
Ln(1)–C(C_8H_8)	2.772(3)	2.652(2)	2.84(3)	2.964(9)
Ln(2)–C(C_8H_8)	2.621(1)	2.665(3)	2.81(3)	2.964(9)
Cnt(1)–Ln(1)–Cnt(2)	145.5	161.2	149.3	137.6
Cnt(3)–Ln(2)–Cnt(2)	170.9	159.2	148.9	137.6

[a] Cnt(1) is the centroid of the C1–C5 ring. [b] Cnt(2) is the centroid of the C21–C28 ring. [c] Cnt(3) is the centroid of the C11–C15 ring.

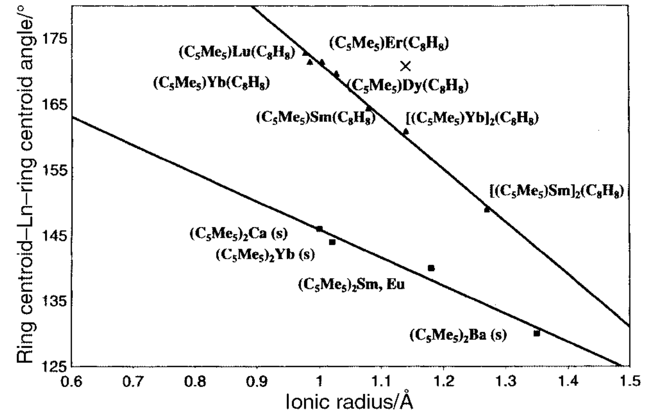

Fig. 2 Graph of ionic radii *versus* (ring centroid)–Ln–(ring centroid) angle. × represents the $(\mu\text{-}C_8H_8)Yb(C_5Me_5)$ angle of the unsolvated half of $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$, **6**.

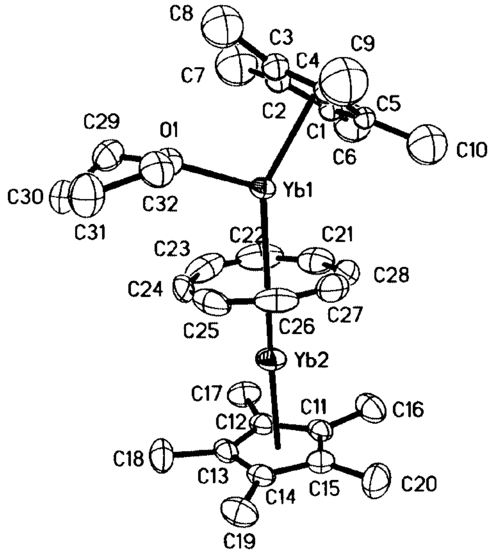

Fig. 3 Thermal ellipsoid plot of $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$, **6**, with ellipsoids drawn at the 50% probability level.

the unsolvated Yb(2)–C(C_5Me_5). This can be compared to the 2.634(4) Å Yb–C(C_5Me_5) distances in the symmetrical unsolvated $[(C_5Me_5)Yb]_2(C_8H_8)$.[9] Since longer bond distances are observed with higher coordination numbers,[21] the longer Yb(1)–C(C_5Me_5) distance is reasonable. The 0.07 Å difference between the solvated and unsolvated sides can be compared to the 0.03 Å difference in Ln–C(C_5Me_5) distances in $(C_5Me_5)_2Sm(THF)$[23] (2.82(4) Å) *versus* $(C_5Me_5)_2Sm$ (2.79(1) Å). The difference is 0.12 Å between $[(C_5Me_5)Sm]_2(C_8H_8)$ (2.79(1) Å) and $[(C_5Me_5)Sm(MeOCH_2CH_2OMe)]_2(C_8H_8)$ (2.910(6) Å), molecules whose metal centers differ by two coordination numbers.

The Yb–C_8H_8 distances show even more disparity than the Yb–C_5Me_5 distances: the solvated Yb(1)–C(C_8H_8) distance is 2.772(3) Å while the unsolvated Yb(2)–C(C_8H_8) distance is 2.621(1) Å, which is similar to the average Yb–C(C_8H_8) distance in unsolvated $[(C_5Me_5)Yb]_2(C_8H_8)$ (2.658(2) Å). In comparison, solvated $[(C_5Me_5)Sm(MeOCH_2CH_2OMe)]_2(C_8H_8)$ has an average Sm–C(C_8H_8) distance of 2.96(1) *versus* 2.82(1) Å in the unsolvated $[(C_5Me_5)Sm]_2(C_8H_8)$. This 0.14 Å difference is similar to that in **6** even though there is a difference of two in the coordination number.

The two (C_5Me_5 ring centroid)–Yb–(C_8H_8 ring centroid) angles in **6** are also significantly different: 145.5° on the solvated side and 170.9° on the unsolvated side. In comparison, the monosolvated $(C_5Me_5)_2Sm(THF)$[23] has a (C_5Me_5 ring centroid)–Sm–(C_5Me_5 ring centroid) angle of 137° which is not so different from the 140.1° in $(C_5Me_5)_2Sm$. The analogous difference between the 137.6° angle in the solvated bimetallic $[(C_5Me_5)Sm(MeOCH_2CH_2OMe)]_2(C_8H_8)$ and the 148.9° and 149.3° angles in $[(C_5Me_5)Sm]_2(C_8H_8)$ is larger, but this difference due to a change in coordination number of two is still not as large as found in **6**.

Discussion

The crystal structures of **1**–**4** are similar to that of **5** and have no unusual bond distances. As such, they comprise a suitable series of compounds for the evaluation of the effect of radial size on the (C_5Me_5 ring centroid)–Ln–(C_8H_8 ring centroid) angle in this mixed ligand C_5Me_5/C_8H_8 system. As shown in Fig. 2, complexes **1**–**5** demonstrate a linear relationship between the (C_5Me_5 ring centroid)–Ln–(C_8H_8 ring centroid) angles and the ionic radii of the lanthanides. Hence, this linear correlation is not limited to the divalent examples of the previously characterized $[(C_5Me_5)Ln]_2(C_8H_8)$ compounds or the $(C_5Me_5)_2M$ complexes. The data on trivalent **1**–**5** fall on the line of data for the divalent $[(C_5Me_5)Ln]_2(C_8H_8)$ species and the slope is similar to that observed for the $(C_5Me_5)_2M$ family of compounds. This suggests that similar factors are operating in these mixed ligand systems and that neither metal oxidation state nor $4f^n$ configuration has strong effects on this angular parameter.

However, the structure of the mixed ligand half-solvated bimetallic complex $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$, **6**, does not fit the trends in Fig. 2 as well as the structures of **1**–**5**. As indicated by the × in Fig. 2, the 170.9° (C_5Me_5 ring centroid)–Yb–(C_8H_8 ring centroid) angle for the unsolvated part of the complex, which is analogous to the other examples in Fig. 2, is not on the other lines. In fact, this 170.9° angle for **6**, which contains divalent ytterbium (Yb(II) ionic radius 1.14 Å), is closer to the 171.5° angle of the trivalent ytterbium complex, **2**, (Yb(III) ionic radius 0.985 Å). This suggests that the (ring centroid)–metal–(ring centroid) angles in bimetallic species may be more flexible and that the substitution of the atoms on the "other" side of the bimetallic complex can have a substantial effect on the structure. Too few data are available to substantiate this indication, but if correct it means that structural variations and their consequent variations in reactivity may be externally manipulated *via* the substitution around a metal center on the other side of a bimetallic complex. In this sense, the $[(C_5Me_5)Yb(THF)(\mu\text{-}C_8H_8)]^-$ component of **6**, which is acting like a monoanionic ligand for the unsolvated Yb(II) center, is affecting the (ring centroid)–Ln–(ring centroid) angle to a greater extent than a single $(C_5Me_5)^-$ ligand.

Conclusion

The structural parameters for the trivalent $(C_5Me_5)Ln(C_8H_8)$ complexes demonstrate a trend similar to that found for the divalent complexes $[(C_5Me_5)Ln]_2(C_8H_8)$ and $(C_5Me_5)_2M$, namely, that bending increases with increasing radial size. These results show that neither f^n configuration nor oxidation state has as strong an effect as radial size on bending in these mixed ligand metallocenes. However, the mixed solvate compound, $[(C_5Me_5)Yb(THF)](\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)[Yb(C_5Me_5)]$, deviates from this regular pattern and suggests that additional data should be pursued on such asymmetric bimetallic systems.

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