error. Intermolecular methyl-methyl, methyl-M, and M-H contacts are also very similar in the two complexes.

Discussion

As discussed in the Introduction, neither simple electrostatic considerations, nor molecular orbital calculations,[17] nor steric effects predict the bent structure observed for metallocenes $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$. From all of these viewpoints, a parallel ring structure like that found in $(C_5Me_5)_2Fe$ might be expected.[46] The similarity of the structures of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ indicates that the bent structure cannot be explained on the basis of the specific $4f^6$ or $4f^7$ electron configuration. The relative 4f electron configurations in these molecules evidently exert no structurally discernible effect. Such a result is consistent with previous observations that the f electron configuration has a minimal effect on the structure of organolanthanide complexes.[13]

It is conceivable that the bent structures of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ result from intermolecular interactions and crystal packing effects. Certainly, some intermolecular distances exist in the crystal which are shorter than normal. The Ln-C(11)′ distance, the shortest of the intermolecular metal carbon contacts, would be the most likely candidate for an interaction with structural consequences. It is curious that this "interaction", if it exists, occurs from the side of the bent structure rather than from the more sterically accessible front end. It is not clear, why such an "interaction" could not occur in a parallel ring structure in which unfavorable intramolecular methyl-methyl contacts would be diminished. In addition, the length of the Ln-C(11)′ distance is sufficiently long that the energy involved is likely to be very small. Since the bent structure leads to short, possibly unfavorable methyl-methyl distances, the reason for bending must have some energetic advantage. Crystal packing effects are also difficult to rationalize into a simple explanation. For example, neither the (ring centroid)-Ln-(ring centroid) angle nor the twist angle, describing the partial staggering of the rings, are such as to minimize intramolecular methyl-methyl distances. It is unlikely that these interactions are the determining factors in giving the observed structure.

Perhaps the best explanation for the bent metallocene structures of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ is the polarization argument used to analyze bent vs. linear MX_2 alkaline-earth-metal dihalide complexes.[25,47] In a parallel ring $(C_5Me_5)_2Ln$ structure analogous to a linear MX_2 structure, polarization of the cation by one C_5Me_5 anion could diminish the electrostatic interaction between the cation and the second C_5Me_5 anion directly opposite. A bent structure may optimize the polarization of a large cation by two anions and may give better total electrostatic bonding for the two rings. This argument provides a nice electrostatic rationale for the bent structures of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ without involving 4f orbital participation and without invoking high-energy 5d and 6s orbitals (via a stereochemically active lone-pair argument).

Acknowledgment. We thank the National Science Foundation for support of this research, the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E.), Professor R. J. Doedens for help with the crystal structure, Professor H. D. Kaesz for helpful discussion, and D. K. Drummond for magnetic measurements.

Registry No. $(C_5Me_5)_2Sm$, 90866-66-3; $(C_5Me_5)_2Eu$, 101200-04-8; $(C_5Me_5)_2Ca$, 101200-05-9; $(C_5Me_5)_2Sm(THF)_2$, 79372-14-8; $(C_5Me_5)_2Eu(THF)$, 74282-45-4; Ca, 7440-70-2; C_5Me_5H, 41539-64-4.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes for $(C_5Me_5)_2Eu$ and $(C_5Me_5)_2Sm$ (26 pages). Ordering information is given on any current masthead page.

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Organolanthanide and Organoyttrium Enolate Chemistry. Synthesis of $[(C_5H_4R)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$ Complexes and the Molecular Structure of $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$

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The reaction of $LiOCH{=}CH_2$ with $[(C_5H_4R)_2LnCl]_2$ (R = H, CH_3; Ln = Lu, Yb, Y) generates the dimeric complexes $[(C_5H_4R)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$ in good yield. $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ crystallizes from toluene under hexane diffusion in space group $P2_1/n$ with unit-cell dimensions $a = 15.793$ (3) Å, $b = 9.983$ (4) Å, $c = 8.257$ (1) Å, $\beta = 93.51$ (1)°, $V = 1300$ (2) Å^3, and $Z = 2$ dimers for $D_{calcd} = 1.483$ g cm^{-3}. Least-squares refinement on the basis of 1518 observed reflections led to a final R value of 0.034. Each $OCH{=}CH_2$ group bridges the two $(CH_3C_5H_4)_2Y$ units through the oxygen atom with Y-O distances of 2.275 (3) and 2.290 (3) Å. The enolate has a C—O distance of 1.324 (6) Å, a C=C distance of 1.287 (8) Å, and an O—C=C angle of 128.0 (6)°. The $[(C_5H_4R)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$ complexes can also be formed by thermolysis of $(C_5H_4R)_2Y(CH_2SiMe_3)(THF)$ (R = H, CH_3) and by thermolysis of $[(C_5H_5)_2YbCH_3]_2$ in the presence of LiCl and THF.

Introduction

In recent years a variety of substituted enolate ligands of the general formula O—CR=CR′R″ have been reported in organolanthanide and organoactinide complexes.[2-7] Most of these are derived from CO activation reactions and representative examples are shown in Chart I. Simple

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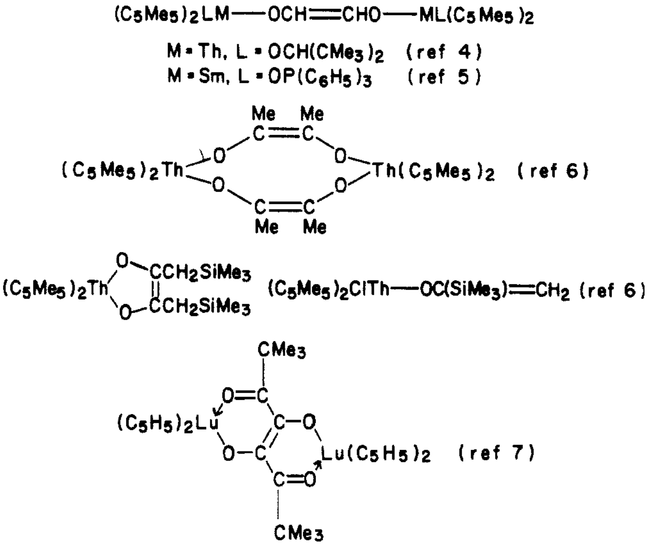
[1] Alfred P. Sloan Research Fellow.

Table I. ^1H NMR Data on Metal Enolate Complexes[a]

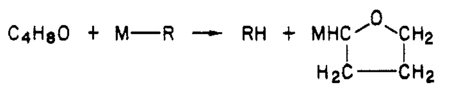
species	(C_5H_4R)	$OCH{=}CH_2$	$OCH{=}CH_2$
$[(C_5H_5)_2Y(\mu\text{-}OCH{=}CH_2)]_2$[b]	6.13 (s)	6.80 (dd, J_t = 12.5 Hz, J_c = 5.4 Hz)	4.16 (dd, J_t = 12.5 Hz, J_{gem} = 1.0 Hz), 4.03 (dd, J_c = 5.4 Hz, J_{gem} = 1.0 Hz)
$[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$[b]	6.07 (dd), 2.10 (s)	6.25 (dd, J_t = 13.5 Hz, J_c = 5.8 Hz)[c]	4.02 (dd, J_t = 13.5 Hz, J_{gem} = 1.0 Hz),[c] 3.93 (dd, J_c = 5.8 Hz, J_{gem} = 1.0 Hz)
$[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$[b,d]	5.87, 5.68, 2.21	6.85 (dd, J_t = 13.8 Hz, J_c = 5.8 Hz)	4.56 (dd, J_t = 13.8 Hz, J_{gem} = 1.0 Hz), 4.48 (dd, J_c = 5.8 Hz, J_{gem} = 1.0 Hz)
$[(C_5H_5)_2Lu(\mu\text{-}OCH{=}CH_2)]_2$[b]	6.13 (s)	5.97 (dd, J_t = 13.8 Hz, J_c = 5.8 Hz)	3.86 (dd, J_t = 13.8 Hz, J_{gem} = 1.3 Hz), 3.95 (dd, J_c = 5.8 Hz, J_{gem} = 1.3 Hz)
$[(C_5H_5)_2Ti(OCH{=}CH_2)_2$[e]	...	7.15 (dd, J_t = 13.6 Hz, J_c = 5.6 Hz)	4.11 (dd, J_t = 13.6 Hz), 3.99 (dd, J_c = 5.6 Hz)
$LiOCH{=}CH_2$[f]	...	6.92 (dd, J_t = 13.4 Hz, J_c = 5.4 Hz)	3.15 (dd, J_t = 13.4 Hz, J_{gem} = 2.0 Hz), 3.60 (dd, J_c = 5.4 Hz, J_{gem} = 2.0 Hz)

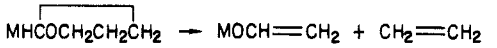
[a] In C_6D_6 except as noted, δ (ppm). [b] This work. [c] Upon decoupling the methylene cis proton, a doublet at δ 6.23 (J = 13.5 Hz) and a singlet at δ 4.02 are observed. [d] In C_4D_8O. [e] Reference 17. [f] Reference 8.

Chart I



enolate ligands such as $OCH{=}CH_2$ have not been reported in f-element complexes, although they could conceivably be generated from the common solvent tetrahydrofuran by metalation as shown in eq 1 and 2.[8] Such a reaction is readily effected by *tert*-butyllithium.[8] The known *tert*-butyllanthanide and -yttrium complexes such as $(C_5H_5)_2Ln(t\text{-}C_4H_9)(THF)$[9,10] and $LiLn(t\text{-}C_4H_9)_4(THF)_4$[11] do not attack THF, although they do participate in metalation reactions.[12,13] However, given the high metalation reactivity reported for some lanthanide complexes,[14] it is likely that organolanthanide enolate formation via eq 1 and 2 will occur in some systems.


(1)


(2)

We report here the synthesis of $OCH{=}CH_2$ lanthanide complexes by the reaction of organolanthanide alkyls with THF and by reaction of organolanthanide chlorides with $LiOCH{=}CH_2$. We also describe the X-ray crystal structure of $[(CH_3C_5H_4)Y(\mu\text{-}OCH{=}CH_2)]_2$, the first structurally characterized simple enolate complex of metals of this type.

Experimental Section

The complexes described below are extremely air and moisture sensitive. Therefore, all syntheses and manipulations of these compounds were conducted under nitrogen with the rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques. The solvents were dried and degassed as previously described.[10] All yttrium and lanthanide starting materials were prepared according to the literature.[10,13,15] $LiOCH{=}CH_2$ was synthesized by reacting $t\text{-}C_4H_9Li$ with THF according to the literature.[8] Physical measurements were made as previously described.[10] NMR spectra were recorded on a Bruker 250-MHz spectrometer in C_6D_6 solution.

Synthesis by Metathesis. $[(C_5H_5)_2Lu(\mu\text{-}OCH{=}CH_2)]_2$. In the glovebox, $[(C_5H_5)_2LuCl]_2$ (0.233 g, 0.34 mmol) was dissolved in 50 mL of THF. $LiOCH{=}CH_2$ (0.034 g, 0.68 mmol) was added in one portion. After the colorless solution was stirred overnight, the solvent was removed by rotary evaporation. The resulting straw-colored solid was extracted with toluene and the extract was filtered and rotary evaporated to dryness. The extraction procedure was repeated two more times to give a straw-colored free-flowing powder (0.140 g, 44%); mp 214–216 °C dec. Anal. Calcd for $LuC_{12}H_{13}O$: Lu, 50.25. Found: Lu, 50.0. ^1H NMR spectral data for all the new complexes are presented in Table I. IR (KBr): 3080 w, 3060 w, 2920 m, 2880 m, 1600 s, 1440 w, 1360 w, 1320 m, 1260 m, 1170 s, 1100 w, 1010 s, 960 s, 770 vs cm^{-1}.

$[(C_5H_5)_2Yb(\mu\text{-}OCH{=}CH_2)]_2$. In an analogous manner, this substance was obtained from $[(C_5H_5)_2YbCl]_2$ as an orange powder in 40% yield; mp 274–278 °C dec. Anal. Calcd for $YbC_{12}H_{13}O$: Yb, 49.97. Found: Yb, 49.50. IR (KBr): 3100 m, 2980 m, 1620 s, 1450 w, 1330 m, 1270 s, 1260 s, 1180 s, 1090 w, 1010 s, 970 m, 770 vs cm^{-1}.

$[(C_5H_5)_2Y(\mu\text{-}OCH{=}CH_2)]_2$. In an analogous manner, this substance was obtained from $[(C_5H_5)_2YCl]_2$ as a white free-flowing

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Table II. Crystal Data for $[(C_5H_4CH_3)_2Y(\mu\text{-}OCH{=}CH_2)]_2$

formula	$C_{28}H_{34}O_2Y_2$
fw	580.39
space group	$P2_1/n$
a, Å	15.793 (3)
b, Å	9.983 (4)
c, Å	8.257 (1)
β, deg	93.51 (1)
V, Å^3	1300 (2)
Z	2 (dimers)
D_{calcd}, g cm^{-3}	1.483
temp, °C	24
λ(Mo Kα)	0.71073 Å; graphite monochromator
μ, cm^{-1}	44.9
transmissn coeff (min–max)	0.571–0.701
type of scan	θ–2θ
scan width	−1.2° in 2θ from $K\alpha_1$ to +1.2° from $K\alpha_2$
scan speed	3.0–12.0°/min, variable
bkgd counting	evaluated from 96-step peak profile
data collectn range	$4° \leq 2\theta \leq 50°$
total unique data	2470
unique data with $I \geq 3\sigma(I)$	1518
no. of parameters refined	157
$R(F)$	0.034
$R_w(F)$	0.042
GOF	1.213
max Δ/σ in final cycle	0.04

powder in 80% yield: mp 123–125 °C. Anal. Calcd for $YC_{12}H_{13}O$: Y, 33.92. Found: Y, 33.2. IR (KBr): 3080 w, 2960 m, 1610 s, 1440 w, 1390 m, 1310 m, 1260 m, 1170 s, 1010 s, 980 s, 780 vs cm^{-1}.

$[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$. In an analogous manner this substance was obtained from $[(CH_3C_5H_4)_2YCl]_2$ as a straw-colored free-flowing powder in 44% yield; mp 114–116 °C. Anal. Calcd for $YC_{14}H_{17}O$: Y, 30.64. Found: Y, 30.0. IR (KBr): 3080 w, 3060 m, 2900 m, 2960 m, 1600 s, 1480 w, 1460 w, 1440 w, 1380 m, 1360 m, 1290 m, 1240 w, 1210 w, 1160 s, 1120 w, 1060 w, 1042 m, 1020 m, 960 s, 920 w, 820 s, 760 vs, 720 w cm^{-1}. X-ray quality crystals of $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ were obtained from slow diffusion of hexane into a saturated toluene solution at −20 °C. The complex sublimes with partial decomposition to $(CH_3C_5H_4)_3Y$ (40% decomposition at 145 °C).

Synthesis by Thermal Decomposition of Alkyl Complexes. $[(C_5H_5)_2Yb(\mu\text{-}OCH{=}CH_2)]_2$. In the glovebox, $[(C_5H_5)_2YbCl]_2$ (2.439 g, 3.36 mmol) was placed in a Schlenk flask equipped with a Teflon stirring bar and dissolved in 100 mL of THF. The vessel was transferred to a Schlenk manifold and cooled to −78 °C. $LiCH_3$ in Et_2O (4.5 mL of 1.6 M, 7.2 mmol) was added by syringe to yield a tomato-red solution. The stirred reaction mixture was allowed to warm to room temperature overnight and returned to the glovebox. The solvent was removed by rotary evaporation to give a viscous oil which was placed in a Soxhlet thimble. Soxhlet extraction under nitrogen on a Schlenk manifold over 14 h in toluene gave an orange solution which was filtered and rotary evaporated to dryness to give an orange free-flowing powder (55%). Anal. Calcd for $YbC_{12}H_{13}O$: C, 41.51; H, 4.09; Yb, 49.97. Found: C, 41.29; H, 4.85; Yb, 49.20. Spectral properties were as described above.

$[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$. A sealed NMR tube containing $(CH_3C_5H_4)_2Y(CH_2SiMe_3)(THF)$ in benzene-d_6 was heated to 85 °C for 5 days. ^1H NMR spectroscopy revealed quantitative generation of $SiMe_4$ (δ 0.00) relative to the total amount of $CH_3C_5H_4$ present. $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$, identified by its characteristic ^1H NMR spectrum, was generated in 64% yield based on the integration.

$[(C_5H_5)_2Y(\mu\text{-}OCH{=}CH_2)]_2$. In an analogous manner, thermolysis of $(C_5H_5)_2Y(CH_2SiMe_3)(THF)$ in an NMR tube at 90 °C for 2 days was found to give a quantitative yield of $SiMe_4$ and a 25% yield of $[(C_5H_5)_2Y(\mu\text{-}OCH{=}CH_2)]_2$. The major product in this case was $(C_5H_5)_3Y(THF)$ (75% yield) based on integration of the C_5H_5 signal.

X-ray Data Collection, Structure Determination, and Refinement for $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$. General procedures for data collection and reduction have been described previously.[16] A clear, well-formed crystal measuring 0.21 × 0.22 × 0.51 mm was sealed under N_2 in a glass capillary and mounted on a Syntex $P2_1$ diffractometer. Lattice parameters were determined at 24 °C from the angular settings of 15 computer-centered reflections with $5° \leq 2\theta \leq 25°$. Relevant crystal and data collection parameters for the present study are given in Table II. Systematic absences ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$) unambiguously established the space group as $P2_1/n$ (alternate setting of $P2_1/c$, no. 14).

Table III. Fractional Coordinates and Their Estimated Errors for $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$

atom	x	y	z	10^4U_{eq},[a] Å^2
Y	0.88516 (3)	0.01267 (4)	1.01870 (5)	405 (3)
O	0.9951 (2)	0.0988 (3)	0.8865 (4)	463 (20)
C(1)	0.9905 (4)	0.1774 (6)	0.7571 (7)	607 (38)
C(2)	1.0494 (5)	0.2505 (7)	0.7021 (9)	758 (47)
C(3)	0.7859 (3)	−0.0220 (5)	0.7494 (6)	547 (31)
C(4)	0.8551 (3)	−0.1087 (6)	0.7392 (6)	571 (35)
C(5)	0.8488 (4)	−0.2073 (5)	0.8588 (7)	645 (38)
C(6)	0.7753 (4)	−0.1810 (5)	0.9413 (7)	629 (38)
C(7)	0.7358 (3)	−0.0688 (5)	0.8726 (6)	548 (33)
C(8)	0.6496 (4)	−0.0158 (7)	0.9130 (8)	852 (47)
C(9)	0.9115 (4)	0.1829 (7)	1.2697 (8)	702 (41)
C(10)	0.8523 (5)	0.0842 (7)	1.3129 (6)	847 (50)
C(11)	0.7771 (4)	0.1008 (6)	1.2203 (8)	744 (46)
C(12)	0.7888 (4)	0.2086 (5)	1.1179 (7)	612 (37)
C(13)	0.8709 (4)	0.2599 (5)	1.1470 (7)	583 (36)
C(14)	0.9057 (5)	0.3811 (6)	1.0656 (9)	1055 (59)
H(1)	0.939 (4)	0.181 (6)	0.694 (7)	541 (196)
H(2a)	1.036 (4)	0.315 (8)	0.605 (8)	839 (245)
H(2b)	1.109 (4)	0.260 (6)	0.755 (8)	720 (235)

[a] $U_{eq} = {}^1/_3$(trace of orthogonalized U_{ij} matrix).

During the data collection, the intensities of three standard reflections measured every 100 reflections exhibited only random fluctuations within ±2%. The structure was solved by using a combination of direct methods (MULTAN 80) and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters using full-matrix least-squares methods. A total of 14 hydrogen atoms, including the three associated with the enolate bridge, were located from difference maps. The rest were placed in calculated positions (C–H = 0.95 Å). The three enolate hydrogens were refined with isotropic temperature factors; cyclopentadienyl hydrogen positions were not refined. A final difference map contained no recognizable features; its largest peak was of height 0.73 e A^{-3} at a distance of 1.06 Å from the yttrium atom. The final values of the positional parameters are given in Table III.

Results and Discussion

Synthesis by Ionic Metathesis. Bis(cyclopentadienyl)lanthanide and -yttrium enolate complexes can be prepared by ionic metathesis from the corresponding chloride and $LiOCH{=}CH_2$ (eq 3). Separation

$$[(C_5H_4R)_2LnCl]_2 + 2LiOCH{=}CH_2 \xrightarrow{THF} 2LiCl + [(C_5H_4R)_2Ln(\mu\text{-}OCH{=}CH_2)]_2 \quad (3)$$

1, R = H, Ln = Y
2, R = H, Ln = Yb
3, R = H, Ln = Lu
4, R = CH_3, Ln = Y

of the LiCl byproduct is achieved by removing the THF solvent, extracting the soluble enolate complex into toluene, and filtering off the insoluble LiCl.

Spectral Characterization. The infrared spectrum of each of the organometallic products of eq 3, 1–4, possesses a strong absorption in the 1600–1620 cm^{-1} region which is attributable to a C=C stretch.[17,18] Each spectrum

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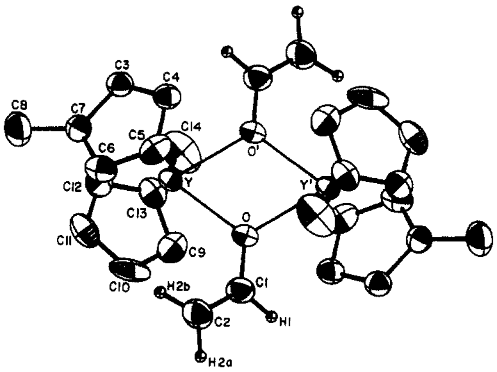

Figure 1. ORTEP plot of the molecular structure of $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$.

Table IV. Bond Distances (Å) in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$

Y–Y′	3.667 (1)	C(3)–C(4)	1.401 (7)
Y–O	2.275 (3)	C(4)–C(5)	1.402 (7)
Y–O′	2.290 (3)	C(5)–C(6)	1.406 (7)
Y–C(3)	2.664 (5)	C(6)–C(7)	1.386 (7)
Y–C(4)	2.624 (5)	C(7)–C(3)	1.406 (7)
Y–C(5)	1.609 (5)	C(7)–C(8)	1.517 (8)
Y–C(6)	2.650 (5)	C(9)–C(10)	1.419 (9)
Y–C(7)	2.709 (5)	C(10)–C(11)	1.383 (9)
Y–C(9)	2.693 (5)	C(11)–C(12)	1.388 (8)
Y–C(10)	2.615 (5)	C(12)–C(13)	1.401 (7)
Y–C(11)	2.609 (5)	C(13)–C(9)	1.396 (8)
Y–C(12)	2.639 (5)	C(13)–C(14)	1.504 (8)
Y–C(13)	2.701 (5)	C(1)–H(1)	0.94 (6)
O–C(1)	1.324 (6)	C(2)–H(2a)	1.04 (7)
C(1)–C(2)	1.287 (8)	C(2)–H(2b)	1.02 (7)

also contains a strong band between 1160 and 1120 cm^{-1} in the C–O stretching region. Absorptions in the 1260–1310 and 1320–1390 cm^{-1} regions may be attributed to in-plane =CH and =CH_2 deformation vibrations, respectively.[17,18]

The ^1H NMR spectra of the diamagnetic yttrium and lutetium systems are consistent with structures in which the oxygen atom of the enolate bonds to the metal center. As shown in Table I, the =CH resonances appear as doublets of doublets with coupling constants comparable to those in the crystallographically characterized titanium complex $(C_5H_5)_2Ti(OCH{=}CH_2)_2$[17] and in $LiOCH{=}CH_2$.[8] The NMR signals due to the =CH_2 protons in complexes **1**, **3**, and **4** appear as two distinctive doublets of doublets, again with coupling constants comparable to those found in $(C_5H_5)_2Ti(OCH{=}CH_2)_2$ and $LiOCH{=}CH_2$. The largest difference in coupling constants is in the geminal coupling: in the $[(C_5H_4R)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$ complexes it is half of the 2-Hz value observed in the lithium enolate. Decoupling experiments on $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ are consistent with the assignments in Table I.

X-ray Crystal Structure of $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$. X-ray analysis of single crystals confirmed the presence of an enolate ligand in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$. As shown in Figure 1, the complex crystallizes as a dimer in which the two cyclopentadienyl rings and the two bridging enolate oxygen atoms coordinate to each yttrium in a roughly tetrahedral geometry. The structure is typical of bent metallocene species which contain two additional ligands.[19] Tables IV and V give the important bond distances and angles.

The average yttrium cyclopentadienyl carbon distance, 2.651 (5) Å, is similar to that found in other trivalent yttrium complexes: $[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$ (**5**),[20] 2.66 (2) Å; $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$ (**6**),[10] 2.69 (2) Å; $[(C_5H_5)_2Y(\mu\text{-}\eta^2\text{-}HC{=}NCMe_3)]_2$ (**7**),[21] 2.68 Å; and $[(C_5H_5)_2Y(\mu\text{-}N{=}CHCMe_3)]_2$ (**8**),[13] 2.64 Å. The (ring centroid)–Y–(ring centroid) angle in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$, 128.1°, is also similar: **5**, 128.9°; **6**, 127.5°; **7**, 127.2°; **8**, 129.7°. The Y–Y′ distance of 3.667 (1) Å is on the long end of the range of Y–Y′ contacts in other yttrium dimers: **5**, 3.599 (8) Å; **6**, 3.664 (1) Å; **7**, 3.607 (1) Å; **8**, 3.617 (2) Å. Consistent with this, the O–Y–O′ angle in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$, 73.12 (12)°, is quite small. Typically, organoyttrium and organolanthanide complexes display X–Ln–Y angles in the range of 79–106°.[22]

Table V. Bond Angles (deg) in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$

O–Y–O′	73.1 (1)	C(3)–C(7)–C(8)	126.6 (5)
Y–O–Y′	106.9 (1)	C(10)–C(9)–C(13)	106.5 (5)
C(1)–O–Y	127.3 (3)	C(9)–C(10)–C(11)	109.6 (6)
O–C(1)–C(2)	128.0 (6)	C(10)–C(11)–C(12)	106.7 (6)
C(4)–C(3)–C(7)	108.3 (5)	C(11)–C(12)–C(13)	109.6 (5)
C(3)–C(4)–C(5)	107.6 (5)	C(12)–C(13)–C(14)	125.2 (6)
C(4)–C(5)–C(6)	107.8 (5)	C(9)–C(13)–C(14)	127.1 (6)
C(5)–C(6)–C(7)	108.5 (5)	(ring centroid)–Y–(ring centroid)	128.1
C(6)–C(7)–C(8)	125.4 (5)		

Comparisons of the yttrium–oxygen distances in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$, 2.275 (3) and 2.290 (3) Å, with related organoyttrium species cannot be made directly, since this is the first crystallographically characterized organometallic yttrium complex containing a metal–oxygen bond. The closest structurally characterized complexes are some organosamarium compounds containing oxygen ligands.[5,23–25] None of these structures involve a single bonded oxygen ligand in a three-center bridge as in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$, so only indirect comparisons can be made. In the samarium oxygen species, Sm–O distances ranging from 2.094 (1) to 2.25 (1) Å are found. Of particular interest are the enediolates $[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-}OCH{=}CHO)$.[5] The cis isomer has Sm–O distances of 2.107 (7) and 2.122 (8) Å; the trans isomer has Sm–O lengths of 2.147 (10) and 2.179 (10) Å. To compare these lengths with those of $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$, the ionic radius of Y^{3+} (0.084 Å smaller than that of Sm^{3+}) as well as the difference in terminal vs. three-center bridging distances must be considered. A recent survey of organoyttrium and organolanthanide chloride complexes has shown that terminal Ln–Cl distances are smaller than bridging Ln–Cl–Ln distances by 0.04–0.27 Å.[26] On the basis of the observed Sm–O distances, a terminal Y–O distance range of 2.01–2.17 Å might be expected. A bridging Y–O–Y distance could then range from as little as 2.05 to as long as 2.44 Å. The observed distances in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ are within this range.

Another related complex that could be compared to $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ is the bis terminal enolate $(C_5H_5)_2Ti(OCH{=}CH_2)_2$.[17] On the basis of the Ti–O distance of 1.903 (2) Å, a terminal Y–O distance of 2.182 Å

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Table VI. Bond Distances (Å) and Angles (deg) in Selected Enolate Complexes

complex	C=C dist	O–C dist	O–C–C angle	M–O–C angle	M–O dist	metal radius[a]	ref
$[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$	1.287 (8)	1.324 (6)	128.0 (6)	127.3 (3)	2.275 (3) 2.290 (3)	1.019	this work
$(C_5H_5)_2Ti(OCH{=}CH_2)_2$	1.306 (5)	1.329 (4)	128.4 (2)	145.5 (2)	1.903 (2)	0.74	17
$[LiOC(CMe_3){=}CH_2]_4(THF)_4$	1.34	1.35	...	...	1.94 1.99	0.59	27
$(C_5H_5)_2ZrCl[OC(SiMe_3){=}CH(9\text{-anthryl})]$	1.334 (7)	1.360 (6)	122.4 (5)	157.7 (3)	1.950 (4)	0.84	34
$(C_5H_5)_2Ti[OC(OC{=}CPh_2){=}CPh_2]$	1.38 (2)	1.36 (2)	122.9 (1)	115.0 (8)	1.92 (1)	0.74	35

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might be anticipated when the difference in metallic radii is considered. One would account for the observed Y–O bond lengths by a lengthening of 0.093–0.108 Å due to bridging versus terminal ligation. This lengthening is within the range observed for lanthanide chloride complexes.[26]

The metrical parameters of the enolate moiety of $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ are compared with those of other metal enolates in Table VI. The enolate C=C distance of 1.287 (8) Å is on the short end of the range of values found in *cis*-$[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-}OCH{=}CHO)$[5] (1.32 (2) Å), in $[(C_5Me_5)_2Th]_2[\mu\text{-}OC(Me){=}C(Me)O]_2$[6] (1.33 (2) Å), in $[LiOC(CMe_3){=}CH_2]_4(THF)_4$[27] (1.34 Å), in $[LiOC(CMe_3){=}CH_2]_6$[28] (1.313 (8) Å), and even in $(C_5H_5)_2Ti(OCH{=}CH_2)_2$ (1.306 (5) Å), which was described as containing an exceedingly short C=C bond length.[17] The C—O bond distance of 1.324 (6) Å is within the range of distances observed in *cis*-$[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-}OCH{=}CHO)]$, 1.32 (2) and 1.35 (2) Å, and is very close to the C–O distance in $(C_5H_5)_2Ti(OCH{=}CH_2)_2$, 1.329 (4) Å.[29] The enolate O—C=C bond angle of 128.0 (6)° is identical within error to that in the titanium enolate of 128.4 (2)°. The dihedral angle between the plane containing the enolate ligand and the plane containing the yttrium atoms and oxygen is 26.5°.

Formation of Enolate Complexes by Thermal Decomposition of Alkyl Species. As part of our systematic study of the hydrogenolysis of Ln–C bonds in organolanthanide alkyl complexes,[15] we needed to prepare substantial quantities of $[(C_5H_4R)_2LnCH_3]_2$ complexes (Ln = Y, Er, Yb, Lu; R = H, CH_3) which were free of the LiCl byproduct of their synthesis (eq 4). LiCl-free complexes

$$[(C_5H_4R)_2LnCl]_2 + 2CH_3Li \xrightarrow{THF} [(C_5H_4R)_2LnCH_3]_2 + 2LiCl \quad (4)$$

were required because hydrogenolysis in the presence of LiCl gives hydride products different[30,31] from those obtained in halide-free reactions.[10,13] Separation of LiCl from the solid reaction mixture obtained by removing the solvent in eq 4 can be achieved to a large extent by extracting the soluble $[(C_5H_4R)_2LnCH_3]_2$ complexes into toluene. Multiple extractions including one with hot toluene are generally needed to remove all of the LiCl, however.[13,15] Soxhlet extraction of the $[(C_5H_5)_2YbCl]_2/CH_3Li$ reaction product was carried out to determine if this would be a more efficient method of separating LiCl. The extract was found to contain not the expected $[(C_5H_5)_2YbCH_3]_2$ but rather the enolate $[(C_5H_5)_2Yb(\mu\text{-}OCH{=}CH_2)]_2$ (eq 5). Metalation of THF by the ytterbium methyl complex according to eq 1 and 2 is a possible route for this reaction.

$$(C_5H_5)_2Yb(CH_3)(THF)/LiCl(THF)_x \xrightarrow[\text{reflux, 72 h}]{\text{toluene}} \underset{55\%}{[(C_5H_5)_2Yb(\mu\text{-}OCH{=}CH_2)]_2} \quad (5)$$

We were interested in determining the generality of this reaction and have examined several other systems. LiCl-free $[(C_5H_5)_2YbCH_3]_2$ in the presence of THF in refluxing toluene will form $[(C_5H_5)_2Yb(\mu\text{-}OCH{=}CH_2)]_2$ in high yield, 90%. $[(C_5H_5)_2LuCH_3]_2$ is not stable under these reaction conditions[32] and forms a variety of products. The lutetium enolate $[(C_5H_5)_2Lu(\mu\text{-}OCH{=}CH_2)]_2$ has not been observed in this system, however. Thermolysis of the $(C_5H_4R)_2Y(CH_3)(THF)$ (R = H, CH_3) complexes in toluene forms $(C_5H_4R)_3Y$ complexes with no evidence for yttrium enolate complexes.[33] However, thermolysis of a sealed NMR scale sample of $(C_5H_5)_2Y(CH_2SiMe_3)(THF)$ in benzene-d_6 generated a quantitative yield of $SiMe_4$ and a 25% yield of the enolate $[(C_5H_5)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ (eq 6). The analogous experiment with the methylcyclopentadienyl derivative $(CH_3C_5H_4)_2Y(CH_2SiMe_3)(THF)$ also generated a quantitative yield of $SiMe_4$ as well as the corresponding enolate $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ in 65% yield.

$$(C_5H_5)_2Y(CH_2SiMe_3)(THF) \xrightarrow[85\ °C]{C_6D_6} [(C_5H_5)_2Y(\mu\text{-}OCH{=}CH_2)]_2 + SiMe_4 \quad (6)$$

These data are consistent with, although not definitive for, a reaction strongly dependent on steric factors. For yttrium complexes the propensity to form enolate complexes follows the order $(CH_3C_5H_4)_2Y(CH_2SiMe_3)(THF) > (C_5H_5)_2Y(CH_2SiMe_3)(THF) > (C_5H_5)_2Y(CH_3)(THF)$ which is also the order of decreasing steric crowding. Likewise, the more sterically crowded $(C_5H_5)_2Yb(CH_3)(THF)$ forms an enolate whereas $(C_5H_5)_2Y(CH_3)(THF)$ does not. $(C_5H_5)_2LuCH_3(THF)$, which is reported to be unstable above 20 °C,[32] may be so sterically crowded that it extrudes THF before a metalation can take place. These data suggest that dramatic effects on reactivity can result from small changes in steric crowding. A similar observation was shown in the study of the hydrogenolysis of Ln–C bonds.[15]

Conclusion

The crystallographic data confirm assignments made from the spectral and chemical evidence that the products

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from thermolysis of $(C_5H_4R)_2Y(CH_2SiMe_3)(THF)$ and $(C_5H_5)_2YbCH_3/LiCl(THF)_n$ and from the reaction of $LiOCH{=}CH_2$ with $[(C_5H_4R)_2LnCl]_2$ are the dimeric lanthanide enolates $[(C_5H_4R)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$. With full characterization of these enolates in hand, formation of organolanthanide enolates in other systems should be readily observable via the distinctive enolate ^1H NMR pattern. Enolate formation should be considered as a possible competing side reaction when lanthanide alkyls are used in THF under harsh conditions.

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Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

Organometallic Compounds of the Lanthanides. 36.[1] Bis(pentamethylcyclopentadienyl) Halide and Alkyl Derivatives of the Lanthanides

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The trichlorides of lanthanum and the lanthanides react with NaC_5Me_5 or KC_5Me_5 in tetrahydrofuran in the presence of ether or dimethoxyethane (dme) with formation of bis(pentamethylcyclopentadienyl)lanthanide halogen complexes of the types $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Na(Et_2O)_2$ (Ln = Pr, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Na(dme)_2$ (Ln = Pr, Gd, Tb, Dy, Ho, Er, Tm), and $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2K(dme)_2$ (Ln = La, Ce). The reactions of these organolanthanide halide complexes with CH_3Li or Me_3SiCH_2Li in the presence of dme or *N,N,N',N'*-tetramethylethylenediamine (tmed) yield $(C_5Me_5)_2Lu(\mu\text{-}CH_3)_2Li(THF)_2$, $(C_5Me_5)_2Ln(\mu\text{-}CH_3)_2Li(tmed)$ (Ln = La, Pr, Lu), and $[Li(dme)_3][(C_5Me_5)_2Ln(CH_2SiMe_3)_2]$ (Ln = Pr, Lu), respectively. The new compounds have been characterized by elemental analyses and IR and NMR spectra. The structure of $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$, which has two slightly different independent molecules per asymmetric unit, has been elucidated through complete X-ray analysis. The crystals are orthorhombic with $a = 16.032$ (11) Å, $b = 16.503$ (6) Å, $c = 25.084$ (9) Å, space group $P2_1ca$, $D(\text{calcd}) = 1.372$ g cm^{-3}, and $R = 0.0476$, for 3240 observed reflections with $I \geq 3\sigma(I)$.

Introduction

Organolanthanides of the type $(C_5H_5)_3Ln$ have been synthesized for all lanthanide metals and for the group IIIB (3[41]) metals scandium, yttrium, and lanthanum. However, dicyclopentadienyllanthanide halides were until recently only known for the heavier lanthanide metals.[2] Using the pentamethylcyclopentadienyl group as a bulky, substituted cyclopentadienyl ligand, Wayda and Evans[3] as well as Tilley and Andersen[4] succeeded for the first time in preparing bis(pentamethylcyclopentadienyl) derivatives of neodymium. Extensive investigations on this class of compounds, including X-ray structural determinations, have been carried out with some bis(pentamethylcyclopentadienyl)ytterbium halides[5-9] as well as some scandium,[10] yttrium,[11,12] samarium,[4] and lutetium analogues.[6,13] Only a few bis(pentamethylcyclopentadienyl)lanthanide alkyl or aryl compounds are in the literature, e.g., $(C_5Me_5)_2ScCH_3$,[10] $(C_5Me_5)_2ScC_6H_5$,[10] $(C_5Me_5)_2ScCH_2C_6H_5$,[10] $(C_5Me_5)_2YCH(SiMe_3)_2$,[12] $(C_5Me_5)_2YC_6H_5$,[12] $(C_5Me_5)_2SmC_6H_5(THF)$,[16] $(C_5Me_5)_2Yb(CH_3)_2Li(Et_2O)_2$,[5] $(C_5Me_5)_2LuCH_3$,[13,14] $(C_5Me_5)_2LuC_6H_5$,[13] $(C_5Me_5)_2LuCH_2SiMe_3$,[13] and $(C_5Me_5)_2Lu(CH_2)_2PMe_2$.[15] Only four of

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