Synthesis and X-ray Crystal Structure of a Dialkyldicyclopentadienylyttrium Complex: {(C₅H₅)₂Y[CH₂Si(CH₃)₃]₂}₂Li₂(CH₃OCH₂CH₂OCH₃)₂(C₄H₈O₂)

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The reaction of [(C₅H₅)₂YCl]₂ with 4 equiv of LiCH₂Si(CH₃)₃ in dimethoxyethane (DME)/dioxane generates LiCl and the complex {(C₅H₅)₂Y[CH₂Si(CH₃)₃]₂}₂Li₂(DME)₂(dioxane), I. Complex I crystallizes from toluene at –20 °C in the triclinic space group $P\bar{1}$ with a = 11.463 (3) Å, b = 11.735 (3) Å, c = 12.262 (4) Å, α = 97.59 (3)°, β = 91.75 (3)°, γ = 112.42 (2)°, and D_{calcd} = 1.179 g cm⁻³ for Z = 1. Least-squares refinement on the basis of 3979 observed reflections led to a final R value of 0.057. The complex crystallizes with two symmetry-related (C₅H₅)₂Y(CH₂SiMe₃)₂⁻ anions, two lithium cations, two DME molecules, and one dioxane molecule in the unit cell. Each yttrium atom is coordinated to two C₅H₅ rings and two CH₂SiMe₃ groups in a pseudotetrahedral arrangement. The average Y–C(ring) distance is 2.69 Å and the average Y–C(CH₂SiMe₃) distance is 2.425 Å. The ring centroid–yttrium–ring centroid angle is 125.4° and the H₂C–Y–CH₂ angle is 97.8°. Each lithium atom is coordinated to three oxygen atoms in a (DME)Li(μ-dioxane)Li(DME) moiety. Each lithium also interacts with a C₅H₅ ring of a (C₅H₅)₂Y(CH₂SiMe₃)₂⁻ unit. I reacts with hydrogen to form the trimeric {[(C₅H₅)₂YH]₃H}⁻ anion.

Currently, the majority of organolanthanide or organoyttrium alkyl complexes described in the literature fall into two major classes:[2-5] the monoalkyl bis(cyclopentadienyl) complexes of the type Cp₂LnR,[6] (Cp₂LnR)₂,[7,8] and Cp₂LnR(THF)[9,10] (Cp = C₅H₅ or C₅H₅₋ₓ(CH₃)ₓ, x = 1, 5) and the homoleptic polyalkyl compounds such as LnR₃,[11,12] LnR₄⁻,[13,14] and LnR₆³⁻.[15-17] Each class has an interesting and rapidly developing chemistry including CO,[18] H–H,[19-21] and C–H[6] activation and polymerization[22] and hydrogenation catalysis.[23] Intermediate between the monoalkyl

complexes and the polyalkyl species should be an extensive class of dialkyl complexes such as (C₅R₅)LnR₂ or (C₅R₅)₂LnR₂⁻ which should also have an interesting chemistry. The first report in the literature of an example of this class involved the dialkynide species (C₅H₅)Ho(C≡CC₆H₅)₂ described in 1975.[6] Subsequently, dimethyl complexes containing other metals such as aluminum and lithium were reported, e.g., (C₅H₅)₂Ln(μ-CH₃)₂Al(CH₃)₂ and (C₅Me₅)₂Ln(μ-CH₃)₂Li(solvent)₂₋₃.[25,26] These complexes can be viewed as Al(CH₃)₃ or LiCH₃ adducts of bis(cyclopentadienyl) lanthanide monoalkyl species. An X-ray crystal structure of (C₅H₅)₂Yb(μ-CH₃)₂Al(CH₃)₂ has been reported,[24] and crystallographic data have been obtained on (C₅Me₅)₂Yb(μ-CH₃)₂Li(THF)₂(Et₂O)[27] and (C₅H₅)₂Er(μ-CH₃)₂Li[(CH₃)₂NCH₂CH₂N(CH₃)₂].[28,29] We report here the first synthesis and X-ray crystal structure of a dialkyl dicyclopentadienyl organolanthanide or organoyttrium complex in which the alkyl groups are not bridging. Given the differences in reactivity commonly observed between terminal and bridging alkyls ligands in complexes of this type,[2,20] this structural type of dialkyl complex should be a desirable addition to this growing class of complexes.[30] The reactivity of this terminal dialkyl complex has been probed with a hydrogenolysis study.

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, all syntheses and subsequent manipulations of these compounds were conducted under nitrogen with the rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques.

Materials. The methods of preparing dry solvents and [(C₅H₅)₂YCl]₂ have been previously described.[19] LiCH₂SiMe₃ was

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $[(C_5H_5)_2Y(CH_2Si(CH_3)_3)_2]_2[Li_2(C_4H_{10}O_2)_2(C_4H_8O_2)]$

compd	$Y_2Si_4Li_2O_6C_{48}H_{92}$
mol wt	1069.26
space group	$P\bar{1}$
cell consts	
a, Å	11.463 (3)
b, Å	11.735 (3)
c, Å	12.262 (4)
α, deg	97.59 (3)
β, deg	91.75 (3)
γ, deg	112.42 (2)
cell vol, Å^3	1506
temp, °C	25 ± 2
molecules/unit cell	1
ρ(calcd), g cm^{-3}	1.179
μ(calcd), cm^{-1}	20.47
transmissn factor range	0.6356–0.7017
radiatn	Mo K$\bar{\alpha}$ (0.710 73 Å), graphite monochromatized
type of scan	θ–2θ
scan width	$1.2 < K\alpha_1, 1.2 > K\alpha_2$
scan rate, deg min^{-1}	variable, 4–12
bkgd counting	evaluated from 96-step peak profile
data collectn range	$0° \leq 2\theta \leq 50°$
data with $I \geq 3\sigma(I)$	3979
no. of parameters refined	280
$R(F)$	0.057
$R_w(F)$	0.076
GOF	2.130
max Δ/σ in final cycle	0.07

Table II. Atomic Positional and Equivalent Isotropic Thermal Parameters for $\{(C_5H_5)_2Y[CH_2Si(CH_3)_3]_2\}_2Li_2(CH_3OCH_2CH_2OCH_3)_2(C_4H_8O_2)^a$

atom	x	y	z	10^4U, Å^2
Y	0.2051 (1)	0.0928 (1)	0.2569 (1)	358 (4)
Li	0.9683 (9)	0.3361 (9)	0.2176 (8)	476 (85)
Si(1)	0.4109 (2)	0.2435 (2)	0.5382 (1)	524 (16)
Si(2)	0.4073 (2)	0.2328 (2)	0.0228 (1)	542 (16)
O(1)	0.9627 (4)	0.4588 (4)	0.3438 (3)	528 (38)
O(2)	0.7779 (4)	0.2629 (4)	0.2260 (3)	521 (37)
O(3)	0.9911 (4)	0.4371 (4)	0.0920 (3)	538 (39)
C(1)	0.2094 (9)	−0.1355 (6)	0.2363 (10)	835 (87)
C(2)	0.2082 (9)	−0.1008 (6)	0.3478 (8)	800 (81)
C(3)	0.0927 (11)	−0.0972 (7)	0.3658 (7)	823 (91)
C(4)	0.0245 (7)	−0.1295 (8)	0.2693 (12)	946 (95)
C(5)	0.0930 (12)	−0.1522 (7)	0.1876 (7)	926 (91)
C(6)	0.1518 (11)	0.2843 (11)	0.2033 (13)	1058 (134)
C(7)	0.1423 (10)	0.2920 (9)	0.3121 (10)	927 (103)
C(8)	0.0436 (15)	0.1976 (15)	0.3295 (9)	1052 (151)
C(9)	−0.0113 (8)	0.1318 (9)	0.2348 (22)	1613 (156)
C(10)	0.0570 (18)	0.1853 (18)	0.1544 (9)	1392 (189)
C(11)	0.3866 (5)	0.2065 (6)	0.3869 (5)	476 (51)
C(12)	0.3193 (11)	0.3388 (12)	0.5948 (7)	1267 (144)
C(13)	0.3552 (13)	0.0997 (9)	0.6070 (7)	1403 (131)
C(14)	0.5801 (8)	0.3377 (11)	0.5971 (7)	1118 (104)
C(15)	0.3167 (6)	0.1001 (6)	0.0895 (5)	526 (57)
C(16)	0.2971 (8)	0.2709 (9)	−0.0724 (7)	939 (99)
C(17)	0.5022 (8)	0.3776 (7)	0.1249 (6)	904 (82)
C(18)	0.5281 (7)	0.2047 (9)	−0.0686 (6)	843 (86)
C(19)	1.0490 (8)	0.5876 (6)	0.3637 (6)	791 (74)
C(20)	0.8353 (7)	0.4436 (7)	0.3578 (6)	680 (74)
C(21)	0.7553 (6)	0.3085 (8)	0.3341 (6)	697 (72)
C(22)	0.6929 (7)	0.1364 (7)	0.1864 (7)	740 (69)
C(23)	1.1096 (6)	0.5221 (7)	0.0674 (6)	659 (66)
C(24)	0.8913 (7)	0.4745 (7)	0.0588 (6)	695 (74)

$^a U_{\text{equiv}} = {}^1/_3$ (trace of orthogonalized U_{ij} matrix).

prepared from ClCH$_2$SiMe$_3$ and Li shot (Aldrich) according to the literature.[31]

Physical Measurements. IR spectra[19] and complexometric analyses[32] were obtained as previously described. ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer at 295 K. Chemical shifts were assigned relative to C$_6$D$_5$H at δ 7.15.

$\{(C_5H_5)_2Y(CH_2SiMe_3)_2\}_2Li_2(DME)_2(dioxane)$, I. Method A. In the glovebox, YCl$_3$ (1.000 g, 5.118 mmol) was suspended in 75 mL of dimethoxyethane (DME) in a 125-mL Erlenmeyer flask equipped with a magnetic stirring bar. LiCH$_2$Si(CH$_3$)$_3$ (0.962 g, 10.24 mmol) was added in small portions over 5 min giving a colorless transparent solution. After the solution was stirred for an additional 5 min, NaC$_5$H$_5$ (0.665 g, 10.24 mmol) was added in portions over 5 min. After the colorless solution was stirred for 30 min, the solvent was removed by rotary evaporation. The resulting white solid was extracted into 70 mL of hot toluene, and the extracts were filtered twice while hot. Upon cooling the solution separated into two layers. Attempts to isolate a solid product at this stage only gave oils. However, solids could be obtained by adding dioxane as follows. The solution volume was reduced to 10 mL, and 2 mL each of DME and dioxane was added. The mixture was stirred for 5 min and rotary-evaporated to dryness giving a pale brown glass. Addition of 30 mL of toluene gave a two-phase solution. The upper yellow layer was decanted from the lower brown layer, and 30 mL of hexane was allowed to diffuse into the solution overnight. Colorless transparent crystals of I (0.464 g, 8%) were obtained in this way. A more convenient synthesis is described below.

Method B. In the glovebox, $[(C_5H_5)_2YCl]_2$ (0.569 g, 1.12 mmol) was dissolved in a dimethoxyethane solution (30 mL) containing a small amount of dioxane (1 mL) in a 125-mL Erlenmeyer flask equipped with a magnetic stirring bar. LiCH$_2$SiMe$_3$ (0.421 g, 4.47

mmol) was added in small portions over 5 min. After the colorless solution was stirred for 1 h, the solvent was removed by rotary evaporation. The resulting solid was extracted with two 50-mL portions of hot toluene. The toluene extracts were filtered, and the solvent was again removed by rotary evaporation. The resulting solid was washed twice with 10-mL portions of hexane to give I as a straw-colored free-flowing powder (0.834 g, 70%). Anal. Calcd for Y$_2$Li$_2$C$_{48}$H$_{92}$Si$_4$O$_6$: Y, 16.63. Found: Y, 16.6.[33] ^{1}H NMR (benzene-d$_6$): δ 6.28 (s, 10, C$_5$H$_5$), 3.33 (br s, 7, C$_4$H$_8$O$_2$), 2.69 (s, 11, (CH$_3$OCH$_2$)$_2$), 2.57 (s, 7, (CH$_3$OCH$_2$)$_2$), 0.45 (s, 21, CH$_2$Si(CH$_3$)$_3$), −0.87 (d, 4, J = 2.8 Hz, CH$_2$SiMe$_3$). IR (KBr, cm^{-1}): 2948 s, 2892 m, 2842 m, 2810 w, 1452 w, 1370 w, 1345 m, 1335 m, 1292 w, 1120 w, 1080 s, 1015 m, 898 w, 860 s, 795 m, 770 s, 715 w, 665 w. X-ray quality crystals were grown by cooling a saturated toluene solution from ~100 to −20 °C over a 2-h period.

X-ray Data Collection, Structure Determination, and Refinement for I. The general procedures followed in data collection and processing have been described.[34] A single crystal measuring approximately 0.45 × 0.45 × 0.75 mm was sealed in a glass capillary under N$_2$ in the glovebox and mounted on a Syntex P2$_1$ diffractometer. Table I provides details of the data collection and refinement. The unit cell lengths and their estimated standard deviations were obtained by least-squares refinement of the setting angles for 15 reflections having 12.7 < 2θ < 24.1°. Three intense reflections were measured every 100 reflections during data collection and showed no appreciable decay. An analytical absorption correction was applied to the intensities of the observed reflections.

The structure was solved with a combination of Patterson and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic temperature factors using full-matrix least-squares methods. The weighting scheme using p = 0.05 has

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(33) Note that the calculated Y percentage for the tris(DME) complex, 16.64, is indistinguishable from that of the bis(DME) dioxane species, and the NMR spectra of I show variable DME/dioxane ratios. Crystallization selects for the bis(DME) dioxane complex.

(34) Sams, D. B.; Doedens, R. J. *Inorg. Chem.* **1979**, *18*, 153–156. Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197–204.

been previously described.[34] Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) on all carbon atoms except the methyl carbon atoms of the $-CH_2SiMe_3$ units. No hydrogen atom positions were refined. A final difference map was featureless, with its largest peak of height 1.66 e Å^{-3} at 1.00 Å from the yttrium atom. Table II gives the final atomic positional and thermal parameters.

Hydrogenolysis of I. I (0.394 g, 0.369 mmol) was dissolved in toluene in a 250-mL flask fitted with a greaseless high vacuum stopcock and a stirring bar. The flask was connected to a vacuum line, cooled to –196 °C, and evacuated. Hydrogen was admitted to the flask, and the vessel was warmed to room temperature. When the hydrogen pressure was 1 atm, the flask was sealed and the solution was stirred. A straw-colored powder slowly deposited in the flask over a 2-week period. The solid was collected by filtration and redissolved in DME. After the DME solution was filtered, diffusion of hexane into the system produced a white microcrystalline solid (0.09 g, 20%) identified as {[(C$_5$H$_5$)$_2$Y(μ-H)]$_3$(μ_3-H)}{Li(DME)$_2$} by ^{1}H NMR spectroscopy.[35] ^{1}H NMR (THF-d_8): δ 5.92 (s, 30, C$_5$H$_5$), 3.43 (s, 9, (CH$_3$OCH$_2$)$_2$), 3.27 (s, 13, (CH$_3$OCH$_2$)$_2$), 0.75 (m, μ-H), –1.05 (m, μ_3-H). The position and splitting pattern for the μ- and μ_3-hydride resonances are almost identical with that found for {[(C$_5$H$_5$)$_2$Y(μ-H)]$_3$(μ-H)}-{Li(THF)$_4$}.[35] at 0.75 ppm, μ_3-H at –1.03 ppm. IR (KBr, cm^{-1}): 3080 m, 2940 m, 2877 m, 1640 w, 1460 w, 1435 w, 1305 m, 1170 m, 1040 m, 1010 s, 850 m, 770 vs, 665 w.

Hydrogenolysis of I (0.164 g, 0.153 mmol) in a toluene/THF mixed solvent (10 mL/2 mL) was also carried out following the procedure described above. After 3 weeks, the solution was rotary evaporated to dryness and the solids were dissolved in THF-d_8. The ^{1}H NMR spectrum showed this solution to be a mixture containing {[(C$_5$H$_5$)$_2$Y(μ-H)]$_3$(μ_3-H)}$^-$ and I in a 2:1 ratio.

Results and Discussion

Synthesis. Addition of 4 equiv of LiCH$_2$SiMe$_3$ to a solution of [(C$_5$H$_5$)$_2$YCl]$_2$ in dimethoxyethane (DME) containing dioxane generates the dialkyl dicyclopentadienyl complex {(C$_5$H$_5$)$_2$Y(CH$_2$SiMe$_3$)$_2$}$_2$Li$_2$(DME)$_2$-(dioxane), I, and LiCl. Complex I can also be formed directly from YCl$_3$ by adding 2 equiv of NaC$_5$H$_5$ followed by two equivalents of LiCH$_2$SiMe$_3$ in DME followed by addition of dioxane in the subsequent workup of the product. Attempts to isolate a (C$_5$H$_5$)$_2$Y(CH$_2$SiMe$_3$)$_2^-$ complex in the absence of dioxane gave oils which had NMR spectra indicating multiple C$_5$H$_5$ and CH$_2$SiMe$_3$ environments.

The ^{1}H NMR spectrum of complex I in benzene-d_6 contained a resonance attributable to CH$_2$Si(CH$_3$)$_3$ at 0.46 ppm and a resonance in the cyclopentadienyl region at δ 6.28 with an intensity ratio of about 2:1 indicating the presence of one (trimethylsilyl)methyl group per one cyclopentadienyl ring. The intensity of the resonance at –0.91 ppm and its doublet structure suggested that it arose due to the methylene protons which were coupled to the yttrium nucleus (J_{YH}^2 = 6.4 Hz).[36] ^{1}H NMR resonances for DME and dioxane were also observed but their intensities were not definitive for either a (C$_5$H$_5$)$_2$Y(μ-CH$_2$SiMe$_3$)$_2$Li(L$_2$) structure (where L is an ether oxygen of DME or dioxane) involving bridging CH$_2$SiMe$_3$ ligands or a structure involving distinct ions such as {(C$_5$H$_5$)$_2$Y-(CH$_2$SiMe$_3$)$_2$]$^-$[Li(L$_4$)]$^+$. An X-ray crystal structure determination resolved this question and demonstrated yet another type of coordination geometry for the lithium cation.

X-ray Crystal Structure. Complex I crystallizes from toluene in space group $P\bar{1}$. The unit cell of this crystal contains two (C$_5$H$_5$)$_2$Y(CH$_2$SiMe$_3$)$_2^-$ anions, two lithium
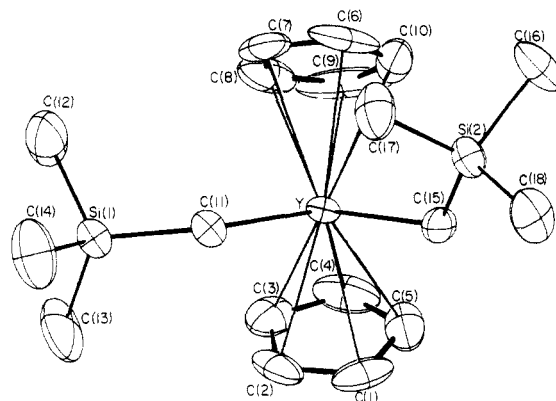

Figure 1. The structure of the anion (C$_5$H$_5$)$_2$Y[CH$_2$Si(CH$_3$)$_3$]$_2^-$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted.
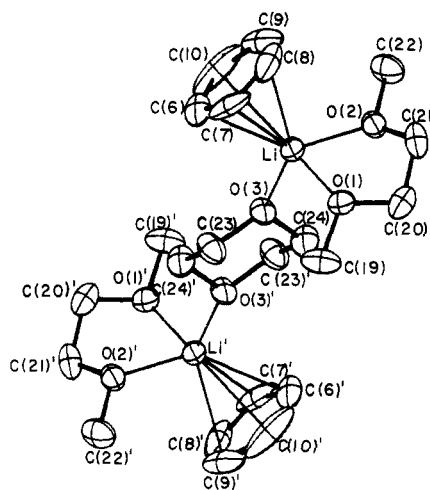

Figure 2. The structure of the cation (DME)Li(μ-dioxane)Li-(DME) including the C$_5$H$_5$ groups which interact with both Li and Y metal centers. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted.

cations, two molecules of DME, and one molecule of dioxane. A crystallographic center of symmetry is located in the middle of the bridging dioxane molecule such that the pairs of anions, cations, and DME molecules are related by inversion. The structure of one of the (C$_5$H$_5$)$_2$Y-(CH$_2$SiMe$_3$)$_2^-$ anions is shown in Figure 1. In each anion, the two cyclopentadienyl ring centroids and the two methylene carbon atoms of the CH$_2$SiMe$_3$ groups define a distorted tetrahedral geometry as is common for bent metallocene complexes which contain two additional ligands.[37] Figure 2 illustrates the coordination geometry of the (DME)Li(μ-dioxane)Li(DME) unit and details the manner in which the cyclopentadienyl rings of the anions are associated with the lithium cations. Each lithium cation is ligated by a bidentate DME molecule, by one end of a bridging dioxane molecule, and by a "bridging" cyclopentadienyl group which is also coordinated to an yttrium atom. Selected bond distances and angles are given in Table III.

Coordination Geometry in the Anion. In the following discussion, the structure of the (C$_5$H$_5$)$_2$Y(CH$_2$SiMe$_3$)$_2^-$ anion will be compared with the structures of other (C$_5$H$_5$)$_2$Ln(X)(Z) complexes (Ln = Y or a lanthanide metal; X, Z = σ-bound ligands) and with that of the actinide bis((trimethylsilyl)methyl) complex (C$_5$Me$_5$)$_2$Th-(CH$_2$SiMe$_3$)$_2$,[38] II.

(35) Evans, W. J.; Meadows, J. H.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4454–4460.

(36) Compare J_{YH}^2 = 3.6 Hz in [(C$_5$H$_5$)$_2$Y(μ-CH$_3$)]^8 and the coupling constants in ref 20.

(37) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742 and references therein.

Table III. Bond Distances (Å) and Angles (deg) for {(C₅H₅)₂Y[CH₂Si(CH₃)₃]₂}₂Li₂(CH₃OCH₂CH₂OCH₃)₂(C₄H₈O₂)

Bond Distances

Y	C(1)	2.677 (7)	Si(2)	C(15)	1.824 (6)
Y	C(2)	2.671 (6)	Si(2)	C(16)	1.907 (8)
Y	C(3)	2.667 (7)	Si(2)	C(17)	1.893 (8)
Y	C(4)	2.668 (7)	Si(2)	C(18)	1.905 (8)
Y	C(5)	2.666 (7)	O(1)	C(19)	1.439 (8)
Y	C(6)	2.696 (7)	O(1)	C(20)	1.421 (8)
Y	C(7)	2.709 (7)	O(2)	C(21)	1.432 (8)
Y	C(8)	2.698 (8)	O(2)	C(22)	1.437 (8)
Y	C(9)	2.701 (9)	O(3)	C(23)	1.415 (8)
Y	C(10)	2.697 (9)	O(3)	C(24)	1.438 (7)
Y	C(11)	2.402 (6)	C(1)	C(2)	1.376 (12)
Y	C(15)	2.445 (6)	C(1)	C(5)	1.377 (13)
Li	O(1)	1.990 (11)	C(2)	C(3)	1.364 (12)
Li	O(2)	2.030 (10)	C(3)	C(4)	1.324 (13)
Li	O(3)	2.029 (10)	C(4)	C(5)	1.352 (13)
Li	C(6)	2.407 (12)	C(6)	C(7)	1.336 (13)
Li	C(7)	2.529 (12)	C(6)	C(10)	1.305 (16)
Li	C(8)	2.618 (13)	C(7)	C(8)	1.294 (14)
Li	C(9)	2.531 (13)	C(8)	C(9)	1.299 (19)
Li	C(10)	2.413 (13)	C(9)	C(10)	1.347 (19)
Si(1)	C(11)	1.836 (6)	C(20)	C(21)	1.481 (10)
Si(1)	C(12)	1.889 (9)	C(23)	C(24)	1.553 (10)
Si(1)	C(13)	1.885 (9)			
Si(1)	C(14)	1.890 (8)			

Bond Angles

Y	C(11)	Si(1)	134.3 (3)	C(6)	C(10)	C(9)	106.6 (10)
Y	C(15)	Si(2)	130.1 (3)	C(7)	C(6)	C(10)	108.2 (10)
Li	O(1)	C(19)	123.6 (5)	C(7)	C(8)	C(9)	108.6 (1)
Li	O(1)	C(20)	110.1 (5)	C(8)	C(9)	C(10)	108.4 (9)
Li	O(2)	C(21)	106.7 (5)	C(11)	Y	C(15)	97.8 (2)
Li	O(2)	C(22)	126.4 (5)	C(11)	Si(1)	C(12)	111.6 (4)
Li	O(3)	C(23)	124.0 (5)	C(11)	Si(1)	C(13)	112.7 (4)
Li	O(3)	C(24)	119.2 (5)	C(11)	Si(1)	C(14)	115.5 (4)
O(1)	Li	O(2)	82.4 (4)	C(12)	Si(1)	C(13)	105.7 (6)
O(1)	Li	O(3)	101.0 (4)	C(12)	Si(1)	C(14)	104.8 (5)
O(1)	C(20)	C(21)	107.9 (5)	C(13)	Si(1)	C(14)	105.9 (5)
O(2)	C(21)	C(20)	107.4 (5)	C(15)	Si(2)	C(16)	110.3 (4)
O(2)	Li	O(3)	103.6 (5)	C(15)	Si(2)	C(17)	113.0 (3)
O(3)	C(23)	C(24)	109.8 (6)	C(15)	Si(2)	C(18)	114.0 (4)
O(3)	C(24)	C(23)	108.7 (6)	C(16)	Si(2)	C(17)	108.9 (4)
C(1)	C(2)	C(3)	108.0 (7)	C(16)	Si(2)	C(18)	105.4 (4)
C(1)	C(5)	C(4)	107.1 (8)	C(17)	Si(2)	C(18)	104.9 (4)
C(2)	C(1)	C(5)	106.8 (8)	C(19)	O(1)	C(20)	112.6 (5)
C(2)	C(3)	C(4)	107.9 (8)	C(21)	O(2)	C(22)	113.0 (5)
C(3)	C(4)	C(5)	110.2 (8)	C(23)	O(3)	C(24)	110.4 (5)
C(6)	C(7)	C(8)	108.2 (9)				

Bond Angles. As shown in Table IV, the ring centroid–Y–ring centroid angle, 125.4°, and the C–Y–C angle formed by the two CH₂SiMe₃ groups and the yttrium atom in I, 97.9°, are both in the range observed for similar angles in other (C₅H₅)₂Ln(X)(Z) complexes. The 125.4° angle is smaller than the ring centroid–Th–ring centroid angle of 134.9° in II as is typical for C₅Me₅ vs. C₅H₅ systems. The C–M–C angle compares well with the corresponding 96.8 (4)° angle in II. The dihedral angle between the plane defined by the two ring centroids and the metal and the plane defined by the metal and the methylene carbon atoms of the CH₂SiMe₃ ligands is 89.0°. For II, a dihedral angle of 89.2° was observed.

Another parameter which describes the coordination geometry of the anion in I is the length of the vectors which run at right angles from the ring centroid–metal–ring centroid plane to the methylene carbon atoms of the CH₂SiMe₃ ligand.[38] If this plane contains a C_2 axis, the vectors to each carbon atom will be equivalent. For I, the distances are 1.72 and 1.93 Å. For the thorium complex II, the difference in these distances is nearly twice as large: the vector lengths are 2.04 and 1.66 Å. Hence, in complex

II the two CH₂SiMe₃ ligands are displaced less symmetrically about the plane than in I. Complex II also has disparate Th–C–Si angles in the two CH₂SiMe₃ ligands: 132.0 (6)° and 148.0 (7)°. In contrast, the analogous angles in complex I are in a more normal range: 130.1 (3)° and 134.3 (3)°. In both I and II, the vectors which lie in the metal–C–Si plane and which bisect the metal–C–Si angles point in the same direction (i.e., ≪ as opposed to toward each other, <>, or away from each other, ><[38]).

The nonequivalence of the CH₂SiMe₃ groups with respect to the ring centroid–metal–ring centroid plane and the large Th–C–Si angle in II were attributed to steric crowding and short methyl–methyl contacts between the methyl groups on the C₅Me₅ rings and on the CH₂SiMe₃ ligands.[38] The structure observed for II, which still had some methyl–methyl contacts shorter than the sum of their van der Waals radii, was thought to be the best compromise in an overall sterically crowded system. Such steric problems are not evident in I which has smaller cyclopentadienyl rings but which also has a metallic radius approximately 0.11 Å smaller.[39] Since the degree of steric congestion often correlates well with reactivity,[20] these two

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Table IV. Bond Distances (Å) and Angles (deg) in $(C_5R_5)_2M(X)(Z)$ Molecules[a]

complex	ring centroid–M–ring centroid	av M–C(ring)	X–M–Z	M–terminal alkyl	ref
Cp$_2$Y(CH$_2$SiMe$_3$)$_2^-$	125.4	2.68 (1), 2.70 (1)	97.9 (2)	2.402 (6) 2.445 (6)	this work
Cp$_2$Lu(t-C$_4$H$_9$)(THF)	125.6	2.63 (1)	106	2.47 (2)	b
[(CH$_3$C$_5$H$_4$)$_2$YbCl]$_2$	126.7	2.585 (7)	82.05 (5)		c
[Cp$_2$Y(CH=NC(CH$_3$)$_3$]$_2$	127.2	2.675 (6), 2.674 (6)	89.9 (4)		d
[Cp$_2$YbCH$_3$]$_2$	128.2	2.613 (13)	93.4 (5)		8
[(CH$_3$C$_5$H$_4$)$_2$Sm(C≡CCMe$_3$)]$_2$	128.6	2.71 (4), 2.72 (4)	83.6 (5)		e
Cp$_2$Lu(C$_6$H$_4$CH$_3$)(THF)	128.8	2.345 (39)	89.6 (12)	2.345 (39)	10
[Cp$_2$YCH$_3$]$_2$	128.9	2.655 (18)	92.3 (3)		8
Cp$_2$Yb(CH$_3$)(THF)	129.1	2.588 (12), 2.612 (11)	94.10 (33)	2.362 (11)	45
[Cp$_2$Y(N=CHCMe$_3$)]$_2$	129.7	2.636 (5), 2.650 (9)	79.8 (3)		20
[Cp$_2$Er(C≡CC(CH$_3$)$_3$]$_2$	130.2	2.62 (2), 2.63 (2)	83.4 (7)		32
Cp$_2$Lu(CH$_2$SiMe$_3$)(THF)	130.2	2.618 (24), 2.594 (25)	95.8 (9)	2.376 (17)	10
Cp$_2$Yb(DME)	131	2.68 (7), 2.69 (6) 2.80 (10), 2.72 (6)	67.2 (9)		f
Cp$_2$Yb(μ-CH$_3$)$_2$Al(CH$_3$)$_2$	133.1	2.629 (27), 2.585 (26)	87.1 (6)		24
(C$_5$Me$_5$)$_2$Th(CH$_2$SiMe$_3$)$_2$	134.9	2.816 (10), 2.796 (10)	96.8 (4)	2.46 (1) 2.51 (1)	38

[a] R = H, CH$_3$; M = lanthanide, actinide, or yttrium; X, Z = alkyl, halide, ether, etc; Cp = C$_5$H$_5$. [b] Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* 1981, 292–293. [c] Baker, E. C.; Brown, L. D.; Raymond, K. N. *Inorg. Chem.* 1975, *14*, 1376–1379. [d] Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* 1983, *2*, 1252–1254. [e] Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* 1983, *2*, 709–714. [f] Deacon, G. B.; MacKinnon, P. I.; Hambley, T. W.; Taylor, J. C. *J. Organomet. Chem.* 1983, *259*, 91–97.

complexes provide important comparative data for probing the effect of various metal ligand combinations on steric crowding.[40]

Bond Distances. The average Y–C(ring) bond distances in I, 2.67 and 2.70 Å, are in the range found for other $(C_5H_5)_2Ln(X)(Z)$ complexes when the differing radial sizes of the metal are taken into consideration (Table IV). The Y–C(CH$_2$SiMe$_3$) distances, 2.402 (6) and 2.445 (6) Å, compare favorably with the metal–CH$_2$SiMe$_3$ distances observed in $(C_5H_5)_2Lu(CH_2SiMe_3)(THF)$,[10] 2.376 (17) Å, and in II,[38] 2.45 (1) and 2.51 (1) Å, when the difference in metallic radii is considered: Y^{3+} is approximately 0.032 Å larger than Lu^{3+} and 0.11 Å smaller than Th^{4+}.[39] In II, the shorter Th–C distance was associated with the larger Th–C–Si angle, and in I this is also the case.

Coordination Geometry in the Cation. Figure 2 shows the arrangement of ligands around both of the lithium atoms in I. Each lithium is surrounded by two oxygen atoms from a bidentate DME ligand, one oxygen atom from a dioxane molecule (which constitutes a bridge between the two lithium atoms), and the back side of a cyclopentadienyl ligand coordinated to yttrium in a $(C_5H_5)_2Y(CH_2SiMe_3)_2^-$ unit. The C$_5$H$_5$ ring centroid and the three oxygen atoms are arranged in a distorted tetrahedral geometry. The O–Li–O angle formed by the oxygen atoms of the bidentate DME ligand is 82.9 (4)°. This angle is comparable to N–Li–N angles in bidentate (CH$_3$)$_2$NC-H$_2$CH$_2$N(CH$_3$)$_2$ (TMEDA) complexes of lithium.[41,42] The O–Li–O angles formed by one oxygen atom of the DME ligand and one oxygen atom of the dioxane are 101.0 (4)° and 103.6 (5)°. The Li–O distances for the DME oxygen atoms are 1.99 (1) and 2.03 (1) Å; the Li–O distance for the dioxane oxygen atom is 2.03 (1) Å. The bond angles and distances within the DME and dioxane molecules are not exceptional.

The C$_5$H$_5$ group coordinates to the lithium cation such that two carbon atoms, C(6) and C(10), are 0.1–0.2 Å closer

to lithium than the other carbon atoms. The Li–C(6) and Li–C(10) distances are 2.407 (12) and 2.413 (13) Å, respectively, while the other Li–C(ring) distances are 2.529 (12), 2.531 (13) and 2.618 (13) Å. These distances can be compared with the lithium–ring carbon atom distances in the η^5-cyclopentadienyl lithium complexes (TMEDA)Li-[C$_5$H$_4$(SiMe$_3$)][41] and (PMDETA)Li[C$_5$H$_3$(SiMe$_3$)$_2$],[43] which range from 2.257 (10) to 2.350 (6) Å. In the lithium indenide complex (TMEDA)LiC$_9$H$_7$,[42] there are three short Li–C distances in the 2.27–2.31 Å range and two longer distances at 2.375 (4) and 2.379 (4) Å. The Li–C distances in I may be longer than those in these simple lithium cyclopentadienyl systems since the C$_5$H$_5$ ring in I is bridging between two metal centers. A similar situation was observed in the structure of (CH$_3$C$_5$H$_4$)(μ-CH$_3$C$_5$H$_4$)Yb(OC$_4$H$_8$)[44] in which Yb–C distances for the terminal CH$_3$C$_5$H$_4$ ring averaged 2.76 Å and the Yb–C distances in the bridging CH$_3$C$_5$H$_4$ averaged 2.87 Å on one side of the ring and 2.91 Å on the other. The Y–C distances for the bridging C$_5$H$_5$ ring in I are slightly longer than those for the nonbridging ring, but the difference is not statistically significant.

Hydrogenolysis Reactivity. The hydrogenolysis reactivity of lanthanide and yttrium metal–carbon bonds has provided considerable insight into the general principles of the organometallic chemistry of these elements.[2,20,45] Accordingly, we have used hydrogenolysis to probe the reactivity of the terminal alkyl ligands in I. In toluene, I reacts rather slowly with an atmospheric pressure of hydrogen. Over a 2-week period an insoluble product, III, is formed which can be filtered and recrystallized from DME. Characterization of this product by IR and ^{1}H NMR spectroscopy indicates that it is a trimer {[(C$_5$H$_5$)$_2$Y(μ-H)]$_3$(μ_3-H)}{Li(DME)$_2$} analogous to the previously studied {[(C$_5$H$_5$)$_2$Y(μ-H)]$_3$(μ_3-H)}{Li(THF)$_4$}.[35] The coupling patterns arising from the seven $I = ^1/_2$ nuclei unit Y$_3$(μ-H)$_3$(μ_3-H) in both complexes are nearly identical.

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Hydrogenolysis of I also occurs at a slow rate in toluene-/THF, a mixed-solvent system which often gives enhanced reactivity for hydrogenolysis. After 3 weeks under hydrogen, approximately one-third of the starting I is left with the $\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}^-$ product.

The formation of the trimer $\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}^-$ rather than the monomer $(C_5H_5)_2YH_2^{-35}$ is consistent with other organolanthanide and organoyttrium chemistry we have studied. Trimeric $Ln_3(\mu_3\text{-}H)$ complexes are often the favored products in hydride-forming reactions in which alkali metal salts are present.[35,45,46]

Complex I reacts with H_2 at a rate slower than that observed for terminal alkyl complexes such as $(C_5H_5)_2Ln(t\text{-}C_4H_9)(THF)$,[19] IV, $(C_5H_5)_2Ln(CH_3)(THF)$,[20,45] V, and $(C_5Me_5)_2Th(CH_2SiMe_3)_2$,[47] II. The slowness of the reaction could be understood if, in solution, the Li cation becomes associated with the CH_2SiMe_3 ligands, making them effectively bridging alkyls. If lithium association is not responsible for the reduced reactivity to hydrogenolysis, an alternative basis for the slow reactivity of I vs. complexes such as II, IV, and V is the negative charge on I.[48] Further studies are needed to establish if this is a general principle of organometallic reactivity for metals of this type.

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(48) Preliminary studies of the reactivity of $Er(t\text{-}C_4H_9)_4$[13] with H_2 indicated a slow rate of hydrogenolysis: Evans, W. J.; Wayda, A. L., unpublished results.

Diene Derivatives of (η⁶-Toluene)Ni(C₆F₅)₂. The Crystal and Molecular Structures of (η⁴-Norbornadiene)Ni(C₆F₅)₂ and (η⁴-1,5-Cyclooctadiene)Ni(C₆F₅)₂

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In order to study the effect of replacing the π-arene ligand in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$ with a diene, the structures of $(\eta^4\text{-}C_7H_8)Ni(C_6F_5)_2$ and $(\eta^4\text{-}C_8H_{12})Ni(C_6F_5)_2$ were determined. $(\eta^4\text{-}C_7H_8)Ni(C_6F_5)_2$ crystallizes in space group $P\bar{1}$ with 2 molecules per unit cell and lattice constants of $a = 10.733(4)$Å, $b = 10.773(4)$Å, $c = 9.154(4)$Å, $\alpha = 113.66(7)°$, $\beta = 95.12(4)°$ and $\gamma = 60.82(2)°$. $(\eta^4\text{-}C_8H_{12})Ni(C_6F_5)_2$ crystallizes in space group $C2/c$ with 4 molecules per unit cell and lattice constants of $a = 18.755(3)$Å, $b = 8.003(1)$Å, $c = 13.698(3)$Å and $\beta = 118.99(1)°$. If the midpoint of the olefin double bonds is taken as the point of attachment to the nickel, then the coordination sphere in both complexes is approximately square planar. Comparison of the bond parameters in these structures to those observed in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$ suggests that the Ni–C_6F_5 bond length is quite sensitive to small changes in the degree of π-back-bonding. A feasible mechanism for small amounts of π-back-bonding is presented.

Introduction

During the past eight years several examples of (π-arene)ML₂ complexes, where M = Fe, Co, and Ni, have been established by X-ray crystallography.[2–8] These structural studies have provided a good deal of insight into the bonding involved in these complexes. Moreover, molecular orbital calculations by T.A. Albright[5] have provided a model to rationalize the structural and chemical observations. Accordingly, the occupancy of the highest occupied molecular orbital (HOMO), which is antibonding with respect to the π-arene ligand, can account for the distortions of the π-arene from planarity and the M–arene bond distances. Thus far it appears that even the lability of the π-arene is related to the nature of this HOMO. Unfortunately, the number of complexes of this type that can be prepared is still quite limited. However, extensive synthetic work aimed at expanding the scope of π-arene complexes is currently ongoing in our laboratory as well as K.J. Klabunde's.

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