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Bis(1,3-dimethylcyclopentadienyl)yttrium Complexes. Synthesis and X-ray Crystallographic Characterization of $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$, $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$, and $[(1,3\text{-}Me_2C_5H_3)_2(THF)Y(\mu\text{-}H)]_2$[1,2]

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YCl_3 reacts with 2 equiv of $K[1,3\text{-}(CH_3)_2C_5H_3]$ in THF to form $(1,3\text{-}Me_2C_5H_3)_2YCl(THF)$. The chloride complex reacts with CH_3Li to form $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$ which crystallizes from toluene in space group $P2_1/c$ with unit cell dimensions $a = 9.267$ (3) Å, $b = 11.780$ (4) Å, $c = 16.255$ (5) Å, $\beta = 127.01$ (4)°, $V = 1417$ (2) Å^3, and $Z = 2$ (two dimers) for $D_{calcd} = 1.36$ g cm^{-3}. Least-squares refinement on the basis of 842 unique observed reflections converged to a final $R = 0.081$. The complex exists as a methyl-bridged dimer with an average Y–C(ring) distance of 2.65 (2) Å and an average Y–C(methyl) distance of 2.61 (2) Å. Hydrogenolysis of $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$ in a THF/hexane mixture followed by recrystallization from toluene gives the hydride complex $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$ which crystallizes in space group $R\bar{3}c$ with unit cell dimensions $a = 12.5281$ (12) Å, $c = 45.594$ (5) Å, $V = 6197$ (1) Å^3, and $Z = 6$ (six trimers) for $D_{calcd} = 1.34$ g cm^{-3}. Least-squares refinement on the basis of 1786 unique observed reflections converged to a final $R = 0.066$. The trimeric structure has three equivalent $(1,3\text{-}Me_2C_5H_3)_2Y$ units connected by hydride bridges. The average Y–C(ring) distances for each ring in the $(1,3\text{-}Me_2C_5H_3)_2Y$ unit are 2.619 (11) and 2.638 (14) Å. $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$ crystallizes from THF as $[(1,3\text{-}Me_2C_5H_3)_2(THF)Y(\mu\text{-}H)]_2$, which crystallizes in space group $P2_1/n$ with unit cell dimensions $a = 17.713$ (7) Å, $b = 10.673$ (4) Å, $c = 8.993$ (7) Å, $\beta = 91.95$ (5)°, $V = 1699$ (2) Å^3, and $Z = 2$ (two dimers) for $D_{calcd} = 1.36$ g cm^{-3}. Least-squares refinement on the basis of 2274 unique observed reflections converged to a final $R = 0.064$. The complex exists as a hydride-bridged dimer with an average Y–C(ring) distance of 2.69 (1) Å, Y–H distances of 2.03 (7) and 2.27 (6) Å, and an Y–O distance of 2.49 (1) Å. The chemical and structural properties of these $1,3\text{-}Me_2C_5H_3$ complexes are compared with those of C_5H_5 and C_5Me_5 analogues.

Introduction

The cyclopentadienide and pentamethylcyclopentadienide ions have played a key role in the development of organometallic chemistry.[3,4] As monoanionic ligands which provide three electron pairs, they often generate unique electronic and steric environments for the metal in which remarkable organometallic chemistry can occur. In the organolanthanide area, these ions have been particularly valuable.[5-9] They allow the common high coordination numbers of 8–10 required by these large metals to be achieved without an excessive buildup of charge on the complex.

Recent developments in organolanthanide chemistry have demonstrated the importance of steric factors in the chemistry of these elements and have shown that reactivity often can be precisely controlled by changing the relative size of the metal vis-a-vis the ligands.[2,5-11] Hence, for a given metal, the chemistry of a C_5H_5 complex may differ from that of the C_5Me_5 analogue due to the larger size of the C_5Me_5 ring.[8,9] For a given class of C_5H_5 complexes, a gradual change in chemistry is often observed as the metal size is varied.

The effects of varying the metal size from La^{3+} (1.061 Å radius[12]) to Lu^{3+} (0.848 Å) have been studied for years.[13] Variations in chemical reactivity as the size of the cyclopentadienyl ligand is changed are not so well documented, however, since only a few types of partially substituted cyclopentadienides have been used with lanthanide metals. These include primarily monosubstituted ligands RC_5H_4 (R = CH_3,[14] $SiMePh_2$,[15] $SiMe_3$,[16] i-Pr[17]), bridged monosubstituted ligands, e.g. $C_5H_4(CH_2)_3C_5H_4$,[18,19] and the one disubstituted species $(Me_3Si)_2C_5H_3$.[20-23] Preliminary

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studies show that the complexes of the latter ligand exhibit chemistry much like that of C_5Me_5 complexes.[9]

In the present report, we describe the synthesis and structure of a series of complexes of the dimethyl-substituted cyclopentadienide ligand $1,3\text{-}Me_2C_5H_3$ and we compare this ligand to other C_5R_5 systems. In this study, yttrium was the metal of choice due to its favorable NMR characteristics.[11,24]

Experimental Section

The complexes described in this paper are air- and moisture-sensitive. Therefore, all syntheses and subsequent manipulations were conducted under nitrogen with Schlenk, vacuum line, and glovebox (Vacuum Atmospheres HE-553 Dri-lab) techniques.

Materials. Toluene and THF were distilled from sodium benzophenone ketyl. Hexane was distilled from sodium–potassium benzophenone ketyl solubilized with tetraglyme. THF-d_8 and benzene-d_6 were vacuum transferred from sodium benzophenone ketyl. Anhydrous yttrium trichloride was prepared from the hydrate (Research Chemicals, Phoenix, AZ) by the method of Taylor and Carter.[25] Hydrogen (Matheson, Prep Grade) and deuterium (Union Carbide, CP grade) were purified by passage through an Alltech Oxytrap. 1,3-Dimethylcyclopentadiene was prepared according to the literature[26] and then was dried over molecular sieves, degassed, and reacted with potassium hydride (Aldrich) in THF to form potassium 1,3-dimethylcyclopentadienide. Methyllithium (1.6 M in Et_2O, Aldrich) was used as received.

Physical Measurements. Infrared spectra were obtained as previously described.[11] ^1H NMR spectra were recorded with a Bruker 250-MHz spectrometer and were referenced to residual β-methylene protons in C_4D_8O (δ 1.79) or to residual aryl protons in C_6D_6 (δ 7.15). One 500-MHz ^1H NMR spectrum was obtained at the Southern California Regional NMR Facility at CalTech. Complexometric analyses were obtained as previously described.[27]

$[(1,3\text{-}Me_2C_5H_3)_2YCl]_n$ (1). In a typical preparation, potassium 1,3-dimethylcyclopentadienide (2.5 g, 19.0 mmol) was added in the glovebox to a stirred solution of YCl_3 (1.85 g, 9.5 mmol) in 50 mL of THF. The solution was stirred overnight and filtered. Removal of solvent from the filtrate by rotary evaporation gave a white solid. This solid was extracted with toluene and the toluene solution was filtered again to remove any residual KCl. Rotary evaporation of the toluene solution yielded 1 (2.35 g, 80%). Anal. Calcd for $C_{14}H_{18}YCl$: Y, 28.6. Found: Y, 27.9. ^1H NMR (C_6D_6) δ 6.05 (s, 1 H, $Me_2C_5H_3$), 6.02 (s, 2 H, $Me_2C_5H_3$), 2.10 (s, 6 H, $Me_2C_5H_3$). IR (KBr) 3070 m, 3030 m, 2900 s, br, 2730 w, 1980 w, 1950 w, 1570 m, 1490 m, 1440 s, 1360 s, 1250 w, 1215 w, 1130 w, 1020 s, 940 m, 800 s, 760 s, 735 m, 690 w cm^{-1}. Isopiestic molecular weight (THF). Calcd for $(Me_2C_5H_3)_2YCl(THF)$: 382.8. Found: 440.

$[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$ (2). Complex 1 (1.84 g, 5.92 mmol) was dissolved in 50 mL of THF in a Schlenk flask equipped with a magnetic stirring bar. The solution was cooled to −78 °C and MeLi (6.51 mmol) was added by syringe to the stirred solution. The stirring reaction mixture was allowed to warm to room temperature overnight. Removal of THF yielded a waxy white solid. The solid was extracted once with hot toluene and three times with hot hexane to remove all LiCl. Rotary evaporation of the final hexane extract yielded 2 (1.03 g, 60%). Crystals suitable for X-ray analysis were grown from a toluene solution by slow evaporation in the glovebox over a 2-day period. Anal. Calcd for $C_{15}H_{21}Y$: Y, 30.6. Found: Y, 29.9. ^1H NMR (C_6D_6): δ 6.03 (s, 2 H, $Me_2C_5H_3$), 5.98 (s, 1 H, $Me_2C_5H_3$), 2.02 (s, 6 H, $Me_2C_5H_3$), −0.80 (t, 3 H, Y-Me). IR (KBr): 2970–2860 s, 1580 w, br, 1500 w, 1440 s, 1365 s, 1260 m, 1175 s, 1130 m, 1090 m, 1030 s, 940 w, 810 s, br, 755 s, 630 m cm^{-1}.

X-ray Crystallography of $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$. General procedures for data collection and reduction have been described previously.[28] A crystal measuring 0.34 × 0.28 × 0.25 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. Data were collected by the θ–2θ scan technique in bisecting geometry. The p factor in the expression[29] for the standard deviation of the observed intensities was given a value of 0.05. Relevant crystal and data collection parameters are given in Table I. During the data collection, the intensities of three standard reflections measured every 100 reflections exhibited only random fluctuations within ±2.5%. An absorption correction was applied. Systematic absences ($0k0$, k odd; $h0l$, l odd) established the space group as $P2_1/c$ (No. 14). Patterson and difference Fourier techniques were used to locate all non-hydrogen atoms which were refined with anisotropic thermal parameters by use of full-matrix least-squares methods. No hydrogen atoms were located. Atomic scattering factors were taken from ref 30. A final difference map contained no recognizable features; its largest peak was of height 1.48 e Å^{-3} at a distance of 1.36 Å from the yttrium atom. Fractional coordinates are given in Table II.

$[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$ (3). Complex 2 (0.95 g, 1.64 mmol) was dissolved in 20 mL of a 1:1 hexane:THF solution in a 250-mL flask equipped with a high vacuum Teflon stopcock and a magnetic stirring bar. The flask was attached to a vacuum line, cooled to −196 °C, and evacuated. The flask was warmed to room temperature and 1 atm of H_2 was admitted. The solution was stirred under H_2 for 36 h forming a saturated solution and a white precipitate. The solvent was removed by rotary evaporation and the solids were washed with hexane leaving 3 (0.680 g, 0.82 mmol, 75%); mp 160 °C (dec). Crystals suitable for X-ray analysis were grown from a toluene solution by slow evaporation over a 2-day period. Anal. Calcd for $C_{14}H_{19}Y$: Y, 32.2. Found: Y, 32.1. ^1H NMR (C_6D_6) δ 6.61 (s, 1 H, $Me_2C_5H_3$), 6.60 (s, 1 H, $Me_2C_5H_3$), 5.93 (s, 1 H, $Me_2C_5H_3$), 1.98 (s, 7 H, $Me_2C_5H_3$ plus (μ-H); even at 500 MHz these peaks overlapped). IR (KBr) 3080 w, 2940–2870 m, 2730 w, 1450 s, br, 1380 m, 1175 w, br, 1135 w, 1040 w, br, 950 w, 815 s, 770 w, 745 m, 670 w, 620 m cm^{-1}.

X-ray Crystallography of $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$. A single crystal measuring 0.5 × 0.4 × 0.4 mm was handled as described above. Lattice parameters were determined from 25 computer-centered reflections. Crystal and data collection parameters are given in Table I. Cell parameters and diffraction symmetry were indicative of the rhombohedral crystal system and systematic absences (hhl, l odd) defined the space group as $R\bar{3}c$ (No. 167) or $R3c$ (No. 161). Intensity statistics favored the noncentrosymmetric group, and no consistent structure model could be found in $R\bar{3}c$. The structure was solved and refined satisfactorily in $R3c$. During the data measurement, the intensities of three standard reflections measured every 100 reflections varied only by ±1%. An empirical absorption correction was applied. A combination of direct methods (MULTAN)[31] and difference Fourier techniques provided the locations of all non-hydrogen atoms. No hydrogen atoms were located. All non-hydrogen atoms were refined with anisotropic thermal parameters using full-matrix, least-squares methods. Refinement included the use of twice the number of unique data (i.e., 2862 observed reflections). Refinement of the other enantiomorphic form of this complex led to a slight increase in the R factor. The largest peak in a final difference map had a height of 1.20 e Å^{-3} and was 0.14 Å from the yttrium atom. Fractional coordinates are given in Table II.

$[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}D)]_3$ (3′). Following the procedure described above, 2 (0.48 g, 0.83 mmol) was treated with D_2 to form

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement of $[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2\text{Y}(\mu\text{-Me})]_2$ (2), $[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2\text{Y}(\mu\text{-H})]_3$ (3), and $[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2(\text{THF})\text{Y}(\mu\text{-H})]_2$ (4)

	2	3	4
formula	$C_{30}H_{42}Y_2$	$C_{42}H_{57}Y_3$	$C_{36}H_{54}O_2Y_2$
mol wt	580.48	828.66	696.65
space group	$P2_1/c$	$R3c$	$P2_1/n$
a, Å	9.267 (3)	12.5281 (12)	17.713 (7)
b, Å	11.780 (4)		10.673 (4)
c, Å	16.255 (5)	45.594 (5)	8.993 (7)
α, deg	90	90	90
β, deg	127.01 (4)	90	91.95 (5)
γ, deg	90	120	90
cell vol, Å^3	1417	6199	1699
Z	2 (dimers)	6 (trimers)	2 (dimers)
D_{calcd}, g/cm^3	1.360	1.34	1.36
temp, °C	24	24	24
λ(Mo Kα), Å	0.71073; graphite monochromator	0.71073; graphite monochromator	0.71073; graphite monochromator
μ, cm^{-1}	41.2	42.6	25.3
min–max transmisstion coeff	0.433–0.657	0.231–0.333	0.681–0.831
type of scan	θ–2θ	θ–2θ	θ–2θ
scan width, deg	-1.2 in 2θ from Kα_1 to $+1.2$ from Kα_2	-1.2 in 2θ from Kα_1 to $+1.2$ from Kα_2	-1.2 in 2θ from Kα_1 to $+1.2$ from Kα_2
scan speed, deg/min	2–12	3	3–16
bkgd counting	evaluated from 96-step peak profile	evaluated from 96-step peak profile	evaluated from 96-step peak profile
data collecn range, deg	$4 \leq 2\theta \leq 45$	$3 \leq 2\theta \leq 45$	$4 \leq 2\theta \leq 55$
total unique data	2011	1786	4254
unique data with $I \geq 2\sigma(I)$	842 ($I > 3\sigma(I)$)	1431	2274
no. of parameters	145	135	184
$R(F)$	0.081	0.066	0.064
$R_w(F)$	0.096	0.070	0.071
GOF	2.755	1.86	1.81
max Δ/σ in final cycle	0.08	0.25	0.04

the analogous deuteride, **3′**, in 72% yield. IR (KBr) 2900 s, 1440 w, 1360 w, 1200 w, br, 1015 s, br, 800 s, br, 740 w cm^{-1}.

$[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2(\text{THF})\text{Y}(\mu\text{-H})]_2$ (4). Recrystallization of **3** from THF at −34 °C overnight yielded **4**. Colorless crystals suitable for X-ray analysis were obtained in this way. Anal. Calcd for $C_{18}H_{27}YO$: Y, 25.5. Found: Y, 25.0. ^{1}H NMR (C_4D_8O) δ 5.89 (s, 1 H), 5.79 (s, 2 H), 2.82 (t, J_{YH} = 28 Hz, 1 H, μ-H), 2.11 (s, 6 H, $Me_2C_5H_3$). ^{13}C NMR (C_4D_8O) 119.9 (s), 113.5 (d, J_{CH} = 137 Hz), 109.9 (d, J_{CH} = 137 Hz), 17.2 (q, J_{CH} = 91 Hz). IR (KBr) 3080 m, 2900 s, br, 2730 m, 1450 s, 1100–1300 s, vbr, 1020 s, 875 s, 800 s, 750 s, 650 s. Removal of solvent by rotary evaporation from a toluene solution of **4** gave **3**.

X-ray Crystallography of $[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2(\text{THF})\text{Y}(\mu\text{-H})]_2$. A single crystal measuring 0.63 × 0.15 × 0.34 mm was handled as described above. Lattice parameters were determined from 15 computer-centered reflections. Crystal and data collection parameters are given in Table I. Systematic absences ($h0l$, $h + l$ odd, $0k0$, k odd) uniquely defined the monoclinic space group as $P2_1/n$ (nonstandard setting of $P2_1/c$, No. 14). During data collection, the intensities of three standard reflections monitored every 100 reflections showed linear decay of 7%; the intensities of the data set were corrected for this decay. An absorption correction was applied. Patterson and difference Fourier techniques provided the locations of all non-hydrogen atoms which were refined with anisotropic thermal parameters using full-matrix least-squares methods. All hydrogen atoms were observed on a difference map and their idealized (C–H = 0.95 Å) positions were included. Only the bridging hydride was refined. The largest peak in a final difference map had a height of 2.64 e Å^{-3} and was 0.86 Å from the yttrium atom. Fractional coordinates are listed in Table II.

$\{[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2\text{Y}(\mu\text{-H})]_3(\mu_3\text{-H})\}\{\text{Li(THF)}_4\}$ (5). If a sample of $[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2\text{Y}(\mu\text{-Me})]_2$ is extracted only once with toluene, it will contain residual lithium. Hydrogenolysis of such a sample (2.12 g) as described above in the preparation of **3** gave a mixture of **3** and **5**. Removal of solvent from this mixture and extraction of the solid with toluene removed the more soluble **3** (1.23 g, ca. 60%). Extraction of the remaining solid with THF gave **5** (0.63 g, ca. 25%). ^{1}H NMR (C_4D_8O) 6.08 (s, 2 H, $Me_2C_5H_3$), 5.54 (s, 1 H, $Me_2C_5H_3$), 2.19 (s, 6 H, $Me_2C_5H_3$), 0.37 (10-line multiplet with average splitting 8 Hz, 1 H, μ_3-H, cf. ref 35). IR (KBr) 3060 m, 2860 s, br, 1435 m, 1355 m, 1290 m, 1270 m, 1150 s, 1120 s, 1065 m, 800 s, 755 m, 720 m, 655 m cm^{-1}.

Results

Bis(1,3-dimethylcyclopentadienyl)yttrium chloride and methyl complexes can be prepared by using the metathetical procedures common in the synthesis of cyclopentadienyl and monomethylcyclopentadienyl analogues[5–9,32] as shown in eq 1 and 2.

$$\mathrm{YCl_3} + 2\mathrm{K}[1,3\text{-}\mathrm{Me_2C_5H_3}] \xrightarrow[-2\mathrm{KCl}]{\mathrm{THF}} (1,3\text{-}\mathrm{Me_2C_5H_3})_2\mathrm{YCl(THF)} \xrightarrow{\text{toluene}} \underset{\mathbf{1}}{[(1,3\text{-}\mathrm{Me_2C_5H_3})_2\mathrm{YCl}]_n} \qquad (1)$$

$$2(1,3\text{-}\mathrm{Me_2C_5H_3})\mathrm{YCl(THF)} + 2\mathrm{MeLi} \rightarrow \underset{\mathbf{2}}{[(1,3\text{-}\mathrm{Me_2C_5H_3})_2\mathrm{Y}(\mu\text{-Me})]_2} + 2\mathrm{LiCl} \qquad (2)$$

Both **1** and **2** are more soluble than their unsubstituted C_5H_5 analogues, but they are not substantially more soluble than the MeC_5H_4 analogues. For example, complex **1** is not soluble in hexane and complex **2** is only slightly soluble in alkanes. Isopiestic measurements show that $(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2\text{YCl}$ exists as a THF adduct in THF. The ^{1}H NMR spectrum of **2** in benzene-d_6 contains a triplet assignable to the methyl bridges ($J_{\text{Y-H}}$ = 3.3 Hz). This is consistent with a dimeric structure in solution although

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Table II. Fractional Coordinates and Their Estimated Errors for $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$ (2) $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$ (3), and $[(1,3\text{-}Me_2C_5H_3)_2(THF)Y(\mu\text{-}H)]_2$ (4)

atom	*x*	*y*	*z*
		Complex 2	
Y(01)	0.3630 (2)	0.1151 (2)	0.4166 (1)
C(01)	0.677 (2)	0.106 (2)	0.596 (1)
C(02)	0.034 (4)	0.138 (3)	0.369 (3)
C(03)	0.097 (3)	0.245 (4)	0.370 (2)
C(04)	0.249 (4)	0.279 (3)	0.477 (3)
C(05)	0.275 (4)	0.186 (3)	0.537 (2)
C(06)	0.148 (5)	0.099 (2)	0.473 (3)
C(07)	−0.125 (3)	0.079 (3)	0.274 (2)
C(08)	0.354 (4)	0.393 (2)	0.517 (2)
C(09)	0.552 (4)	0.193 (5)	0.355 (2)
C(10)	0.482 (8)	0.081 (3)	0.301 (4)
C(11)	0.280 (5)	0.114 (4)	0.230 (2)
C(12)	0.271 (8)	0.220 (4)	0.250 (4)
C(13)	0.406 (6)	0.277 (3)	0.320 (3)
C(14)	0.736 (4)	0.261 (3)	0.431 (2)
C(15)	0.138 (5)	0.040 (3)	0.149 (2)
		Complex 3	
Y(01)	0.15709 (7)	0.46694 (7)	0.40630 (0)
C(01)	0.1325 (16)	0.3226 (16)	0.4516 (3)
C(02)	0.0127 (13)	0.2901 (10)	0.4414 (2)
C(03)	−0.0115 (10)	0.3787 (11)	0.4471 (2)
C(04)	0.0842 (15)	0.4763 (14)	0.4596 (3)
C(05)	0.1795 (14)	0.4463 (20)	0.4627 (3)
C(06)	0.1908 (25)	0.2454 (26)	0.4498 (4)
C(07)	−0.1384 (24)	0.3718 (32)	0.4413 (4)
C(08)	0.0810 (21)	0.2908 (13)	0.3669 (3)
C(09)	−0.0177 (21)	0.3191 (13)	0.3691 (3)
C(10)	0.0167 (22)	0.4347 (20)	0.3595 (3)
C(11)	0.1322 (17)	0.4765 (13)	0.3494 (3)
C(12)	0.1877 (15)	0.4100 (16)	0.3528 (3)
C(13)	0.0718 (23)	0.1810 (15)	0.3722 (4)
C(14)	−0.0690 (24)	0.5104 (29)	0.3587 (5)
		Complex 4	
Y(01)	0.9114 (1)	0.4112 (1)	1.0141 (1)
O(01)	0.9237 (3)	0.2517 (5)	0.8142 (6)
C(01)	0.7609 (4)	0.4180 (8)	0.9487 (9)
C(05)	0.7957 (5)	0.4494 (9)	0.8171 (9)
C(04)	0.8310 (5)	0.5657 (9)	0.8340 (9)
C(03)	0.8149 (4)	0.6106 (7)	0.9771 (10)
C(02)	0.7743 (4)	0.5183 (8)	1.0472 (8)
C(06)	0.7105 (5)	0.3058 (9)	0.9749 (12)
C(07)	0.8346 (5)	0.7372 (8)	1.0377 (12)
C(08)	0.9054 (5)	0.2008 (8)	1.1805 (10)
C(12)	0.9799 (5)	0.2478 (9)	1.1999 (10)
C(11)	0.9768 (5)	0.3606 (10)	1.2759 (8)
C(10)	0.9020 (5)	0.3857 (8)	1.3065 (8)
C(09)	0.8572 (5)	0.2879 (8)	1.2474 (9)
C(13)	0.8816 (8)	0.0750 (9)	1.1206 (15)
C(14)	0.8747 (6)	0.4955 (11)	1.3959 (10)
C(15)	0.8713 (7)	0.1688 (14)	0.7417 (20)
C(16)	0.9071 (8)	0.0892 (12)	0.6440 (16)
C(17)	0.9793 (7)	0.1441 (11)	0.6188 (12)
C(18)	0.9831 (8)	0.2399 (16)	0.7303 (19)

it does not preclude the existence of a trimer in solution in which distant Y–H coupling is small. A 3.6-Hz coupling was observed in the analogous $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$ system.[33]

Hydrogenolysis of $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$ in a 1:1 mixture of THF and hexane forms a hydride complex in a reaction analogous to hydrogenolyses of C_5H_5 and MeC_5H_4 lanthanide alkyl complexes.[11] The exact product isolated in this reaction depends on how the crude hydrogenolysis product subsequently is treated. Removal of solvent and recrystallization from toluene give trimeric $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$, eq 3. Recrystallization of this

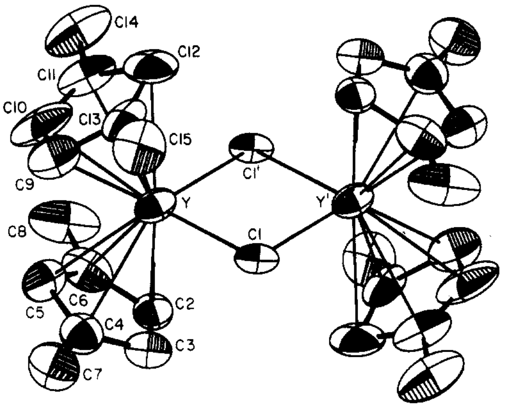

Figure 1. ORTEP plot of the centrosymmetric molecular structure of $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$. Thermal ellipsoids are shown at the 35% probability level.

material from THF gives dimeric $[(1,3\text{-}Me_2C_5H_3)_2(THF)Y(\mu\text{-}H)]_2$, eq 4. This process is readily reversed; removal of solvent from a toluene solution of 4 gives 3.

$$\underset{\textbf{2}}{[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2} + 2H_2 \xrightarrow{THF} \xrightarrow[\text{extraction}]{\text{toluene}} \underset{\textbf{3}}{[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3} \quad (3)$$

$$2\underset{\textbf{3}}{[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3} + 6THF \rightarrow 3\underset{\textbf{4}}{[(1,3\text{-}Me_2C_5H_3)_2(THF)Y(\mu\text{-}H)]_2} \quad (4)$$

A third variation of the hydrogenolysis reaction results when residual lithium salts are present. As has been observed previously,[34] lithium salts can be retained in samples of bis(cyclopentadienyl)lanthanide alkyl complexes unless multiple extractions with hot arene solvents are carried out. $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$ follows this pattern. Extraction with hot toluene and hot hexane is necessary to obtain a lithium-free product. If lithium is present in 2, hydrogenolysis gives a mixture of 3 and the anionic trimer $\{[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}\{Li(THF)_4\}$ (**5**).

The dimethylcyclopentadienyl hydride complexes 4 and 5 are considerably more soluble than their corresponding cyclopentadienyl and methylcyclopentadienyl analogues. For example, $[(C_5H_5)_2(THF)Y(\mu\text{-}H)]_2$[11] is only slightly soluble in THF whereas 4 is very soluble in THF and moderately soluble in toluene. Complex 5 is slightly soluble in toluene whereas its analogue, $\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}\{Li(THF)_4\}$ (**6**),[35] is not. Complex 3, which has no C_5H_5 or MeC_5H_4 analogue, is moderately soluble in toluene.

The ^1H NMR spectrum of 4 in THF-d_8 contains a triplet at δ 2.82 ppm which is assignable to the bridging hydride in this dimeric complex. The observed coupling constant, $J_{Y\text{-}H}$ = 28 Hz, is very close to the 27-Hz value found for the complexes $[(C_5H_4R)_2(THF)Y(\mu\text{-}H)]_2$[36] (R = H, Me) and suggests that 4 is a dimer in solution. The μ-H resonances in 5 are obscured by THF resonances, but the μ_3-H resonance at 0.37 ppm is a well-defined multiplet like that observed in **6**. Unfortunately, in the trimeric 3 the hydride resonances have the same chemical shift as the protons of the methyl group on the dimethylcyclopentadienyl ligand (δ 1.98). Therefore, no conclusion on the structure of 4 in

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[33] Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54–61.

[34] Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2015–2017.

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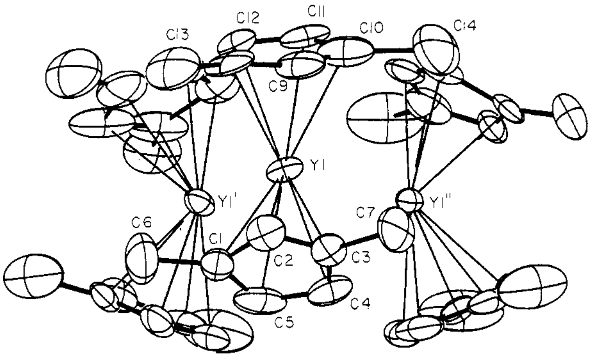

Figure 2. ORTEP plot of the molecular structure of $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$. Thermal ellipsoids are shown at the 30% probability level. The primed atoms are related to the unprimed atoms by a molecular 3-fold axis.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$ (2)

Y(01)–C(01)	2.60 (1)	C(02)–C(03)	1.39 (4)
Y(01)–C(01′)	2.62 (2)	C(03)–C(04)	1.49 (3)
Y(01)–C(02)	2.67 (2)	C(04)–C(05)	1.39 (3)
Y(01)–C(03)	2.60 (2)	C(05)–C(06)	1.43 (3)
Y(01)–C(04)	2.65 (3)	C(06)–C(02)	1.43 (3)
Y(01)–C(05)	2.66 (2)	C(09)–C(10)	1.50 (4)
Y(01)–C(06)	2.65 (2)	C(10)–C(11)	1.55 (5)
Y(01)–C(09)	2.66 (2)	C(11)–C(12)	1.31 (5)
Y(01)–C(10)	2.73 (2)	C(12)–C(13)	1.26 (5)
Y(01)–C(11)	2.65 (3)	C(13)–C(09)	1.49 (5)
Y(01)–C(12)	2.62 (3)	C(02)–C(07)	1.52 (4)
Y(01)–C(13)	2.65 (3)	C(04)–C(08)	1.55 (3)
Y(01)–Y(01′)	3.58 (1)	C(09)–C(14)	1.59 (4)
		C(11)–C(15)	1.46 (4)

C(01)–Y(01)–C(01′)	93.4 (4)	C(06)–C(02)–C(07)	129.2 (38)
Y(01)–C(01)–Y(01′)	86.6 (4)	C(09)–C(10)–C(11)	96.8 (27)
C(02)–C(03)–C(04)	110.7 (28)	C(10)–C(09)–C(14)	141.3 (41)
C(02)–C(06)–C(05)	109.3 (26)	C(12)–C(11)–C(10)	106.6 (33)
C(03)–C(02)–C(06)	105.8 (28)	C(12)–C(11)–C(15)	129.5 (56)
C(03)–C(02)–C(07)	125.0 (37)	C(12)–C(13)–C(09)	99.9 (43)
C(03)–C(04)–C(08)	129.4 (35)	C(13)–C(09)–C(10)	112.9 (28)
C(04)–C(05)–C(06)	109.6 (26)	C(13)–C(09)–C(14)	105.4 (45)
C(05)–C(04)–C(03)	104.5 (28)	C(13)–C(12)–C(11)	123.7 (58)
C(05)–C(04)–C(08)	126.0 (31)	C(15)–C(11)–C(10)	123.5 (52)

solution can be made from these data. However, the observation of three distinct $Me_2C_5H_3$ resonances in the ^1H NMR spectrum suggests that the inequivalence of these cyclopentadienyl hydrogens in the solid-state structure is retained in solution, probably via a nonmonomeric structure. The presence of hydride ligands in 3 is observed in the IR spectrum which shows a strong absorption band at 1450 cm^{-1}. This band is absent in the spectrum of the corresponding deuteride which exhibits a strong absorption at 1015 cm^{-1} ($\nu_{Y-H}/\nu_{Y-D} = 1.43$).

Crystal Structures. Figures 1, 2, and 3 show ORTEP plots of the molecular structures of **2**, **3**, and **4**, respectively. In all cases the $(1,3\text{-}Me_2C_5H_3)_2Y$ unit adopts a bent metallocene[37] geometry in which two or three additional ligands are coordinated to the metal. The structures of **2** and **4** are analogous to those of $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$[33] and $[(MeC_5H_4)_2(THF)Y(\mu\text{-}H)]_2$.[36]

As shown in the bond distance and angle tables, Tables III–V, and in Table VI, which compares data on the $1,3\text{-}Me_2C_5H_3$ complexes **2** and **4** and their C_5H_5 or MeC_5H_4 analogues, the Y–C(ring), Y–O, Y···Y, Y–C(Me), and Y–H distances in the dimethyl substituted systems are similar to those in the less substituted analogues. The Y–Z–Y and

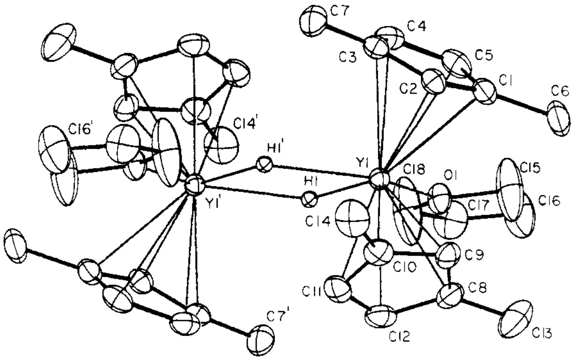

Figure 3. ORTEP plot of the centrosymmetric molecular structure of $[(1,3\text{-}Me_2C_5H_3)_2Y(THF)(\mu\text{-}H)]_2$. Thermal ellipsoids are shown at the 30% probability level.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$ (3)

Y(1)–C(01)	2.659 (10)	C(01)–C(06)	1.48 (2)
Y(1)–C(02)	2.595 (10)	C(02)–C(03)	1.32 (2)
Y(1)–C(03)	2.609 (10)	C(03)–C(04)	1.34 (2)
Y(1)–C(04)	2.619 (10)	C(03)–C(07)	1.57 (2)
Y(1)–C(05)	2.614 (15)	C(04)–C(05)	1.43 (3)
Y(1)–C(08)	2.627 (11)	C(08)–C(13)	1.34 (2)
Y(1)–C(09)	2.654 (16)	C(08)–C(09)	1.45 (3)
Y(1)–C(10)	2.665 (15)	C(08)–C(12)	1.56 (2)
Y(1)–C(11)	2.623 (15)	C(09)–C(10)	1.36 (2)
Y(1)–C(12)	2.623 (11)	C(10)–C(11)	1.35 (2)
C(01)–C(02)	1.42 (2)	C(10)–C(14)	1.75 (3)
C(01)–C(05)	1.45 (2)	C(11)–C(12)	1.33 (2)

C(02)–C(01)–C(05)	103.1 (11)	C(13)–C(08)–C(09)	126.2 (20)
C(02)–C(01)–C(06)	126.2 (18)	C(13)–C(08)–C(12)	130.4 (21)
C(05)–C(01)–C(06)	130.6 (20)	C(09)–C(08)–C(12)	102.8 (12)
C(03)–C(02)–C(01)	110.4 (11)	C(10)–C(09)–C(08)	112.5 (20)
C(02)–C(03)–C(04)	112.1 (12)	C(11)–C(10)–C(09)	103.3 (20)
C(02)–C(03)–C(07)	125.1 (17)	C(11)–C(10)–C(14)	127.6 (20)
C(04)–C(03)–C(07)	122.8 (17)	C(09)–C(10)–C(14)	129.0 (23)
C(03)–C(04)–C(05)	106.7 (14)	C(12)–C(11)–C(10)	120.7 (16)
C(04)–C(05)–C(01)	107.6 (13)	C(11)–C(12)–C(08)	100.4 (14)

Table V. Selected Bond Distances (Å) and Angles (deg) for $[(1,3\text{-}Me_2C_5H_3)_2(THF)Y(\mu\text{-}H)]_2$ (4)

Y(01)–H(01)	2.03 (7)	C(04)–C(05)	1.396 (12)
Y(01)–H(01)′	2.27 (6)	C(05)–C(01)	1.394 (11)
O(01)–Y(01)	2.491 (5)	C(08)–C(09)	1.417 (17)
Y(01)–C(01)	2.711 (7)	C(09)–C(10)	1.405 (11)
Y(01)–C(02)	2.710 (7)	C(10)–C(11)	1.388 (12)
Y(01)–C(03)	2.743 (7)	C(11)–C(12)	1.386 (12)
Y(01)–C(04)	2.686 (8)	C(12)–C(08)	1.417 (12)
Y(01)–C(05)	2.694 (7)	C(01)–C(06)	1.517 (12)
Y(01)–C(08)	2.703 (8)	C(03)–C(07)	1.494 (11)
Y(01)–C(09)	2.77 (8)	C(08)–C(13)	1.502 (13)
Y(01)–C(10)	2.654 (7)	C(10)–C(14)	1.510 (13)
Y(01)–C(11)	2.644 (7)	C(15)–C(16)	1.391 (16)
Y(01)–C(12)	2.677 (8)	C(16)–C(17)	1.432 (17)
C(01)–C(02)	1.404 (10)	C(17)–C(18)	1.432 (14)
C(02)–C(03)	1.384 (10)	C(15)–O(01)	1.424 (12)
C(03)–C(04)	1.411 (11)	C(18)–O(01)	1.321 (13)
		H(01)–H(01)′	2.24 (12)

C(05)–C(01)–C(02)	106.4 (8)	C(10)–C(11)–C(09)	108.2 (8)
C(05)–C(01)–C(06)	127.0 (8)	C(10)–C(11)–C(14)	125.5 (9)
C(02)–C(01)–C(06)	126.3 (8)	C(09)–C(11)–C(14)	126.2 (8)
C(01)–C(05)–C(04)	109.3 (7)	C(11)–C(09)–C(08)	108.0 (7)
C(05)–C(04)–C(03)	107.3 (7)	C(16)–C(15)–O(01)	111.4 (11)
C(02)–C(03)–C(04)	107.3 (7)	C(15)–C(16)–C(17)	106.2 (9)
C(02)–C(03)–C(07)	126.6 (8)	C(16)–C(17)–C(18)	101.7 (9)
C(04)–C(03)–C(07)	126.0 (8)	O(01)–C(18)–C(17)	116.6 (10)
C(03)–C(02)–C(01)	109.5 (7)	C(18)–O(01)–C(15)	101.5 (8)
C(09)–C(08)–C(12)	106.8 (8)	H(01)–Y(01)–H(01)′	62.3 (27)
C(09)–C(08)–C(13)	125.1 (9)	Y(01)′–H(01)–H(01)′	64.2 (30)
C(12)–C(08)–C(13)	127.6 (9)	Y(01)–H(01)–Y(01)	117.7 (27)
C(10)–C(12)–C(08)	108.4 (8)	H(01)′–H(01)–Y(01)	53.4 (25)
C(12)–C(10)–C(11)	108.6 (8)		

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[37] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

Table VI. Selected Bond Distances (Å) and Angles (deg) for Some Trivalent Bis(cyclopentadienyl)yttrium Complexes

	C_5H_5[a]	MeC_5H_4[b]	1,3-$Me_2C_5H_3$[c]
	$[(ring)_2Y(\mu\text{-}Me)]_2$		
Y–C(ring) (av)	2.655 (18)		2.66 (3)
Y–C(Me)	2.545 (11)		2.60 (1)
Y···Y	3.53		3.58 (1)
	$[(ring)_2(THF)Y(\mu\text{-}H)]_2$		
Y–C(ring) (av)		2.69 (2)	2.69 (1)
Y–O(THF)		2.46 (1)	2.49 (1)
Y–(μ-H)		2.17 (8)	2.03 (7)
		2.19 (8)	2.27 (6)
Y···Y		3.66 (1)	3.68 (1)
	$[(ring)_2Y(\mu\text{-}H)]_3$		
Y–C(ring) (av)			2.619 (11)
			2.638 (14)
Y···Y			4.10 (1)

[a] Reference 33. [b] Reference 36. [c] This work.

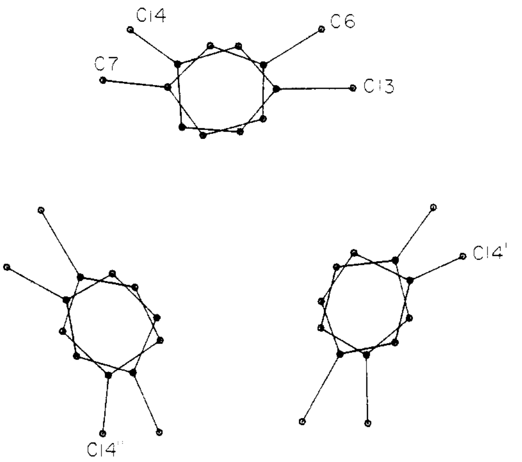

Figure 4. View down the C_3 axis of $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$ showing arrangement of methyl substituents.

Z–Y–Z angles (Z = H, or C(Me)) are also similar. The Y–Z and Y···Y distances for the dimethyl-substituted systems are generally slightly longer as might be expected for a more sterically crowded system.

In contrast to **2** and **4**, $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$ has no analogue in C_5H_5 or MeC_5H_4 chemistry. It is the first neutral trimeric yttrium hydride. The most closely related crystallographically characterized organolanthanide species are the neutral trimer $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$[38] and the anionic systems $\{[(CH_2)_2Er(\mu\text{-}H)]_2[(C_5H_5)_2Er(\mu\text{-}Cl)](\mu_3\text{-}H)\}\{Li(THF)_4\}$ (**7**) and $\{[(C_5H_5)_2Lu(\mu\text{-}H)]_3(\mu_3\text{-}H)\}\{Li(THF)_4\}$ (**8**).[34] As shown in Figure 4, the three crystallographically equivalent $(1,3\text{-}Me_2C_5H_3)_2YH$ units are arranged such that the methyl substituents within a unit are partly staggered and are as far apart as possible between units.

The metal–metal distances in **3** differ significantly from those in **2**, **4**, **7**, and **8**. The nonbonding Y···Y distance of 4.10 (1) Å is much longer than the analogous distances in **2** and **4** (Table VI) and the 3.69 (1), 3.93 (1), and 3.613 (1) Å Ln···Ln distances found in **7** and **8**. $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ is another case of a neutral trimer with a long Ln···Ln distance. It has a 5.63-Å Sm···Sm distance compared to a 3.9-Å separation in $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$.[39] It is possible that the electrostatic attraction of the central μ_3-hydride ligands in **7** and **8** holds the metal centers closer together in the anionic trimers. Neutral trimers can be much more spread out and should be more favorable structures for sterically bulky systems.

Another unusual feature of complex **3** is that the average Y–C(ring) distances for each of the rings in the $(1,3\text{-}Me_2C_5H_3)_2YH$ unit, 2.619 (11) and 2.638 (14) Å, are shorter than those usually seen in cyclopentadienyl yttrium complexes of this type. This shorter ring distance may be a result of the lower coordination number, eight in complex **3**, compared to the coordination number of nine in other hydride complexes of yttrium and the late lanthanide metals.

Discussion

Dimethyl substitution of the cyclopentadienyl ring apparently has little effect on the chemistry of bis(cyclopentadienyl) halide and methyl complexes of yttrium. $[(1,3\text{-}Me_2C_5H_3)_2YCl]_n$ and $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$ are slightly more soluble than their C_5H_5 or $Me_3C_5H_4$ analogues, but the change is not enough to make the chloride soluble in hexane. The structure of **2** is very similar to that of its C_5H_5 analogue. Given the correlations of structure and reactivity for complexes of this type,[2,5–11] it is not surprising that the reactivity of **2** is similar to that of $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$ and $[(MeC_5H_4)_2Y(\mu\text{-}Me)]_2$. Clearly, **2** behaves more like the latter two complexes than like the C_5Me_5 derivatives $[(C_5Me_5)_2LuMe]_x$, $x = 1, 2$.[8,40–43] In the latter case, the steric bulk of the C_5Me_5 rings prevents a symmetric $Lu_2(\mu\text{-}Me)_2$ unit from forming.[8] As a result, more reactive terminal Lu–Me moieties are present which have chemistry different from the μ-Me ligands.[9] The dimethyl-substitution pattern does not destroy the $Ln_2(\mu\text{-}Me)_2$ system and therefore gives chemistry analogous to the $[(RC_5H_4)_2Ln(\mu\text{-}Me)]_2$ complexes (R = H, CH_3). The dimethyl-substitution pattern also has little effect on hydrogenolysis reactivity, which can often be very sensitive to steric factors.[2]

The hydride complex $[(1,3\text{-}Me_2C_5H_3)_2(THF)Y(\mu\text{-}H)]_2$ is also structurally similar to its C_5H_5 and MeC_5H_4 analogues. The four cyclopentadienyl ring centroids do not adopt the tetrahedral geometry found in $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$[39] and $[(C_5Me_5)_2ThH(\mu\text{-}H)]_2$[44] but are closer to the square-planar geometry found in the smaller ring hydrides $[(MeC_5H_4)_2(THF)Ln(\mu\text{-}H)]_2$ (Ln = Er, Y).[36] However, the increased steric crowding caused by the methyl groups in nine-coordinate **4** does affect the chemistry. Specifically, the THF is very easily removed to form the unsolvated hydride, $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$. Desolvation of $[(RC_5H_4)_2(THF)Y(\mu\text{-}H)]_2$ (R = H, Me) is not accomplished so easily. Facile extrusion of THF due to steric crowding has been observed previously in other complexes of this general type. For example, in each of the following pairs of analogues, $(MeC_5H_4)_2Lu(CMe_3)(THF)$[36] and $(C_5H_5)_2Lu(CMe_3)(THF)$[45] and $[(MeC_5H_4)_2(THF)Er(\mu\text{-}H)]_2$ and $[(MeC_5H_4)_2(THF)Lu(\mu\text{-}H)]_2$,[36] the sterically more crowded molecule desolvates more readily.

The result of this enhanced desolvation reactivity in **4** is the facile formation of the trimeric hydride, **3**, a molecule which has no precedent in organolanthanide or organotransition chemistry. This molecule is unusual in that it

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formally appears to be sterically unsaturated. Clearly, the $(1,3\text{-}Me_2C_5H_3)_2YH$ unit can accommodate nine coordination as is demonstrated in $[(1,3\text{-}Me_2C_5H_3)_2(THF)Y(\mu\text{-}H)]_2$. The nine-coordinate structure must be slightly crowded as evidenced by the facile THF loss, but an eight-coordinate structure in which two of the ligands are hydrides probably does not provide optimum steric saturation. As a result, **3** contains shorter Y–C(ring) distances and the molecule is not as thermally stable in solution as **4**. Hence with a dicyclopentadienyl hydride ligand set, dimethyl substitution does perturb the metal–ligand size balance enough to change the chemistry from that observed with C_5H_5 or MeC_5H_4 analogues. The result is a new type of bis(cyclopentadienyl)metal hydride trimer.

Conclusion

Dimethyl substitution of a cyclopentadienyl ring provides a small perturbation to the chemistry of trivalent bis(cyclopentadienyl)yttrium complexes. For chloride and methyl complexes, no structural or chemical consequences are evident. For hydride complexes, the steric balance is affected to a greater extent such that nine-coordinate dimeric species desolvate to form a new class of eight-coordinate trimers. As expected the change is not as great as that caused by substituting the ring with two Me_3Si groups. Hence, the $1,3\text{-}Me_2C_5H_3$ ligand constitutes an intermediate sized cyclopentadienyl ligand which can be used to manipulate organoyttrium and organolanthanide chemistry.

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Registry No. 1, 109959-98-0; 2, 109959-99-1; 3, 109960-00-1; 3′, 109960-02-3; 4, 109960-01-2; 5, 109975-37-3; YCl_3, 10361-92-9; potassium 1,3-dimethylcyclopentadienide, 109929-94-4.

Supplementary Material Available: Tables of thermal parameters (4 pages); a listing of structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

Electrochemical Studies of the Cation Radical $(\eta\text{-}MeC_5H_4)(CO)(MeOH)FeCOMe^+$

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The oxidations of $(\eta\text{-}Cp)(CO)_2FeMe$ ($Cp' = MeC_5H_4$) in methanol and mixtures of methanol and acetonitrile have been studied by a combination of electrochemical, spectroscopic, and chemical techniques. The distribution of $(\eta\text{-}Cp)(CO)(MeOH)FeCOMe^+$ and $(\eta\text{-}Cp')(CO)(AN)FeCOMe^+$ formed during the oxidation of $(\eta\text{-}Cp')(CO)_2FeMe^0$ at low temperatures is initially kinetically determined and reflects the solvent composition. These observations coupled with the computer simulation of cyclic voltammetry experiments show that the acetonitrile and methanol complexes are formed with equal rate constants. We interpret this to be consistent with the intermediacy of a highly reactive species, possibly $(\eta\text{-}Cp')(CO)FeCOMe^+$. The methanol and acetonitrile complexes interconvert in the iron(III) state via an entering ligand-dependent pathway with an equilibrium constant ($K_{eq}(III) = 60$) favoring the acetonitrile complex; however, in the iron(II) state $K_{eq}(II) = 3.5 \times 10^5$.

Introduction

The dramatic kinetic and thermodynamic promotion of the alkyl to acyl migratory insertion reaction that occurs upon oxidation of alkyl transition-metal carbonyls is a well-documented phenomenon.[1,2] Several mechanisms have been proposed to account for the distribution of products, but the origins of these enhancements remain obscure.[3] In order to gain further insight about the behavior of intermediates generated by the oxidation of alkyl iron carbonyls, we studied the oxidation of $(\eta\text{-}Cp')(CO)_2FeMe$[4] in methanol and mixed methanol/acetonitrile at low temperatures.

Results

The generation and ligand exchange reactions of the complex $(\eta\text{-}Cp')(CO)(MeOH)FeCOMe^+$ have been studied by a combination of chemical and electrochemical techniques. The chemical oxidation of $(\eta\text{-}Cp')(CO)_2FeMe$ with ceric ammonium nitrate (Ce(IV)) in alcohols at −78 °C affords deep green solutions that are characteristic of the presence of cation radicals of the type $(\eta\text{-}Cp')(CO)LFeCOMe^+$.[1] The rapid attenuation of the green color as the soluions warmed to room temperature attests to the kinetic instability of the chromophoric species. Consonant with these observations, the cyclic voltammograms (CV's) of $(\eta\text{-}Cp')(CO)_2FeMe$ in MeOH at 22 °C show only the irreversible oxidation ($E_{pa} = 1.25$ V) of the complex; no appreciable concentrations of new electrochemically active species were detected upon scan reversal. These results

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