Inorg. Chem. **2005**, *44*, 7960–7969

Inorganic Chemistry

Article

Methyl Displacements from Cyclopentadienyl Ring Planes in Sterically Crowded $(C_5Me_5)_3M$ Complexes

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Received July 7, 2005

The displacements of the methyl substituents away from the metal and out of the cyclopentadienyl ring plane are compared in sterically crowded $(C_5Me_5)_3M$ complexes vs sterically normal f-element complexes in an attempt to evaluate the utility of this parameter in predicting unusual $(C_5Me_5)^{1-}$ ring reactivity. The out-of-plane displacements of 16 sterically crowded tris(cyclopentadienyl) complexes of general formula $(C_5Me_5)_3M$, $(C_5Me_4R)_3M$ (R = Et, ^{i}Pr, ^{t}Bu, $SiMe_3$), $(C_5Me_5)_3MX$ (*X* = anion), and $(C_5Me_5)_3ML$ (L = neutral ligand) are compared with $[(C_5Me_5)_2U]_2(C_6H_6)$, $(C_5Me_5)_2Sm(PC_4H_2{}^tBu_2)$, and 33 representative examples of f-element bis(cyclopentadienyl) complexes with normal cyclopentadienyl behavior and coordination numbers ranging from 6 to 10. In general, the methyl displacement values of sterically crowded complexes overlap with those in the other complexes, which demonstrates that the basis of the structural distortions is complex. However, if the most extreme out-of-plane displacement in each of the sterically crowded complexes is examined vs the analogous maximum out-of-plane displacement in less crowded systems, there appears to be a basis for predicting cyclopentadienyl reactivity.

Introduction

The synthesis and crystallographic characterization of the first tris(pentamethylcyclopentadienyl) metal complex, (η^5-$C_5Me_5)_3Sm$,[1] was surprising since it was assumed from all previous data that the cone angle of a $(C_5Me_5)^{1-}$ ring was much larger than the 120° required for a $(\eta^5\text{-}C_5Me_5)_3M$ complex.[2] One way to reduce the effective cone angle of a ligand is to locate it further away from the metal.[3] This was indeed the situation for $(C_5Me_5)_3Sm$: all 15 Sm−C bonds were long compared to those in previously characterized $(C_5Me_5)^{1-}$ complexes of Sm^{3+}. The existence of a molecule in which all of the metal−ligand bonds were longer than conventional was in itself surprising. This was especially unusual for the relatively ionic lanthanides: previous surveys of structurally characterized f-element organometallic complexes had shown that metal−ligand bond distances tend to vary only with the size of the metal.[4] The isolation of this sterically crowded $(C_5Me_5)_3Sm$ complex demonstrated that molecules with considerably longer bonds evidently had enough electrostatic stabilization to exist.

Following the discovery of $(C_5Me_5)_3Sm$, some 15 additional examples of complexes containing three pentasubstituted cyclopentadienyl rings have been isolated and crystallographically characterized. These include $(C_5Me_5)_3M$[1,5−8] and $(C_5Me_4R)_3M$[7,9] (R = Et, ^{i}Pr, $SiMe_3$) complexes, as well as compounds with an additional fourth ligand such as $(C_5Me_5)_3MX$[10−12] (X = anion) and $(C_5Me_5)_3ML$[13,14] (L = neutral ligand). All of the metal−ligand distances in these

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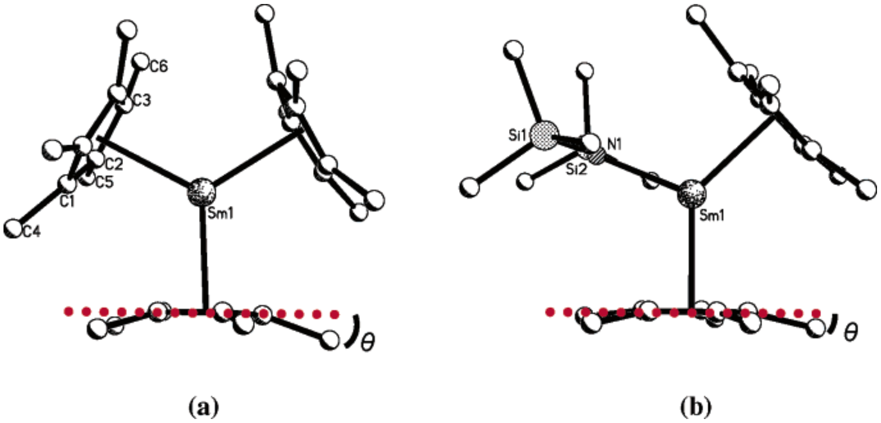

Figure 1. Ball and stick representations of (a) $(C_5Me_5)_3Sm$ and (b) $(C_5Me_5)_2Sm[N(SiMe_3)_2]$ in orientations that highlight the out-of-plane methyl substituent displacements and the angle θ, defined in eq 1, from the average ring carbon plane.

complexes are also unusually long. More importantly, all of these compounds except one, $(C_5Me_5)_3ThH$[12] (to be discussed later), have unusual chemistry associated with their $(C_5Me_5)^{1-}$ ligands.[3,8,15] This includes η^1-alkyl reactivity such as olefin polymerization, CO insertion, and hydrogenolysis, as well as $(C_5Me_5)^{1-}/(C_5Me_5)$ reduction reactivity. The existence of these molecules raises the possibility that other classes of compounds with unconventionally long metal−ligand bonds and unconventional ligand reactivity could also exist.

Visual examination of the structures of $(C_5Me_5)_3M$,[1,5−8] $(C_5Me_4R)_3M$,[7,9] $(C_5Me_5)_3MX$,[10−12] and $(C_5Me_5)_3ML$[13,14] always reveals that the methyl groups are displaced away from the metal center and out of the plane of the five ring carbon atoms, Figure 1a. This type of perturbation also provides a way to reduce the cone angle. For example, in $(C_5Me_5)_3Sm$, the values are 0.18, 0.36, and 0.52 Å. However, out-of-plane displacements of the methyl groups in $(C_5Me_5)^{1-}$ f-element complexes with conventional M−C(C_5Me_5) distances are also observed,[16−49] as shown in Figure 1b for $(C_5Me_5)_2Sm[N(SiMe_3)_2]$.[31] In this complex, the displacements are 0.15, 0.19, and 0.33 Å. Hence, some of the displacements in sterically crowded complexes are no larger than in complexes with normal bond distances and angles. Indeed, the positions of the substituents on cyclopentadienyl groups in metallocenes have been studied extensively both experimentally and theoretically for years,[50−54] and the effect on structure and reactivity of the ratio of metal size to ligand size in cyclopentadienyl complexes of electropositive metals has been reviewed.[4,55,56]

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Table 1. Displacements (Å) for the Three Unique Methyl Substituents from the Average Ring Carbon Plane of the $(C_5Me_5)^{1-}$ Ligand, the C(Me)−C(ring)−(average ring carbon plane) Angles, θ (deg), and the Metal−C(ring) Distances (Å) for $(C_5Me_5)_3M$, $(C_5Me_5)_3MX$, and $(C_5Me_5)_3ML$ Complexes[a]

compound	C(4)	C(6)	C(5)	θ[C(4)]	θ[C(6)]	θ[C(5)]	M−C(1)	M−C(3)	M−C(2)
$(C_5Me_5)_3UCl$[10]	0.54	0.36	0.20	20.9	13.6	7.8	2.899(9)	2.818(8)	2.780(6)
$(C_5Me_5)_3UF$[10]	0.54	0.34	0.16	20.8	12.9	6.4	2.907(7)	2.830(5)	2.790(5)
$(C_5Me_5)_3U(CO)$[13]	0.53	0.34	0.25	20.8	13.1	9.7	2.927(3)	2.847(2)	2.821(2)
$(C_5Me_5)_3U(N_2)$[14]	0.53	0.34	0.24	20.7	13.0	9.4	2.927(4)	2.823(2)	2.848(3)
$(C_5Me_5)_3Sm$[1]	0.52	0.36	0.18	20.3	14.0	6.7	2.910(3)	2.813(3)	2.782(2)
$(C_5Me_5)_3UMe$[11]	0.52	0.35	0.21	20.2	13.5	8.1	2.904(6)	2.802(4)	2.832(4)
$(C_5Me_5)_3Nd$[6]	0.52	0.34	0.17	20.2	13.1	6.6	2.927(2)	2.815(1)	2.842(1)
$(C_5Me_5)_3Pr$[8]	0.52	0.33	0.17	20.0	12.8	6.4	2.938(3)	2.856(2)	2.830(2)
$(C_5Me_5)_3U$[5]	0.52	0.34	0.18	19.9	13.0	6.8	2.920(3)	2.813(3)	2.840(3)
$(C_5Me_5)_3ThH$[12]	0.51	0.31	0.20	19.8	11.9	7.6	2.946(3)	2.872(2)	2.845(2)
$(C_5Me_5)_3Ce$[8]	0.50	0.32	0.17	19.5	12.5	6.4	2.954(2)	2.876(2)	2.850(2)
$(C_5Me_5)_3La$[7]	0.50	0.31	0.16	19.4	11.9	6.1	2.975(3)	2.873(2)	2.896(2)

[a] As shown in Figure 3, the C(1), C(3), and C(2) ring carbons are bound to C(4), C(6), and C(5), respectively. Compounds are listed in order of decreasing maximum out-of-plane displacement. When these are equal, the order is determined by decreasing maximum θ values.

Although some information on the methyl displacements in $(C_5Me_5)^{1-}$ complexes is in the literature, it is scattered in a way that precludes a comprehensive comparison. To determine if there was a pattern in this displacement data that would be useful in making predictions on cyclopentadienyl reactivity, we report here a detailed summary of the out-of-plane methyl displacements for sterically crowded f-element complexes[1,5−14,16,17] and compare the results with methyl displacements for the $(C_5Me_5)^{1-}$ and $(C_5Me_4R)^{1-}$ ligands in complexes that have more conventional bond lengths.[16−49]

Results

Presentation of Data. Tables 1−3 list the out-of-plane displacements (Å) of the methyl substituents for all of the $(C_5Me_4R)^{1-}$ ligands in this study, as well as the C(Me)−C(ring)−(average ring carbon plane) angle which is defined as θ (deg), according to eq 1, Figure 1.

$$\theta = \arcsin\left(\frac{\text{C(Me) displacement from the average ring plane}}{\text{C(Me)}-\text{C(ring) bond distance}}\right) \quad (1)$$

An alternative measure of angular deviation is the C(Me)−C(ring)−(C_5Me_4R ring centroid) angle. These values scale approximately as θ as defined here but are more variable when the $(C_5Me_4R)^{1-}$ rings are distorted. For example, if a ring carbon of the cyclopentadienyl ligand is distorted out of the plane, the C(Me)−C(ring)−(C_5Me_5 ring centroid) angle is not representative of the angle of the methyl displacement from the average ring plane.

For each complex in Tables 1 and 2, the individual entries of the crystallographically unique methyl carbons of each complex are listed in order of decreasing out-of-plane displacement. The complexes in each table are also listed in order of decreasing maximum out-of-plane displacement values. Consequently, the maximum out-of-plane displacements are in the upper left-hand corner of each table. In cases where the maximum displacements were equal, the maximum displacements of the second rings were compared to determine which compound is listed first. When the maximum displacements were equal between highly symmetric complexes having crystallographically equivalent rings and the maximum displacements, the compounds were ordered by decreasing θ values.

Table 1 summarizes the out-of-plane methyl displacements of all the structurally characterized $(C_5Me_5)_3M$,[1,5−8] $(C_5Me_5)_3MX$,[10−12] and $(C_5Me_5)_3ML$[13,14] complexes reported to date. All five ring carbons were used to generate the average ring planes for these complexes. However, only three methyl displacements are shown for each compound in the table since all of these complexes crystallize in the highly symmetric space group $P6_3/m$ and have only three crystallographically independent methyl groups. For these compounds, the M−C(ring) distances associated with each methyl substitutent are also listed to show how the methyl displacements and angles correlate with the M−C(ring) bond distances.

To aid in analyzing the data, Figure 2 lists the maximum, minimum, and median value for all of the complexes analyzed. Since there are only three crystallographically independent methyl groups for the tris(pentamethylcyclopentadienyl) complexes, Figure 2 shows all of the data for these complexes.

Table 2 summarizes out-of-plane methyl displacements for all the rest of the complexes in this study, which include some less-symmetrical sterically crowded compounds and 33 less-crowded complexes. Since most of these compounds have lower symmetry than those in Table 1, more individual measurements are needed to describe their methyl displacements and only displacements and θ values are given in Table 2. For these less-symmetrical complexes, Figure 2 summarizes the data by showing the maximum and minimum displacement, as well as the median value of the out-of-plane displacements. A summary of all the data in Figure 2 is given in Table 3.

Table 2 contains the out-of-plane methyl displacements for all of the structurally characterized $(C_5Me_4R)_3M$ (R = Et,[7,9] ^iPr,[7] ^tBu,[7] $SiMe_3$[7]) complexes in the literature, as well as two sterically crowded bis(pentamethylcyclopentadienyl) complexes, $[(C_5Me_5)_2U]_2(C_6H_6)$[16] and $(C_5Me_5)_2Sm(PC_4H_2{}^tBu_2)$.[17] $[(C_5Me_5)_2U]_2(C_6H_6)$ has unusually long M−C(C_5Me_5) distances, as well as unusual $(C_5Me_5)^{1-}$ reactivity, while

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Table 2. Displacements (Å) for the Methyl Substituents from the Average Ring Carbon Plane Generated by the $(C_5Me_4R)^{1-}$ Ligand and the (average ring carbon plane)−C(ring)−C(Me) Angles, θ (deg), for Selected Tris- and Bis(cyclopentadienyl) Complexes[a]

compound	C(a)	C(b)	C(c)	C(d)	C(e)	θ[C(a)]	θ[C(b)]	θ[C(c)]	θ[C(d)]	θ[C(e)]
$[C_5Me_4(SiMe_3)]_3La$[7]										
ring 1	0.54	0.36	0.31	0.24		21.1	14.0	12.0	9.0	
ring 2	0.46	0.37	0.28	0.27		17.7	14.2	10.7	10.3	
ring 3	0.45	0.34	0.31	0.19		17.3	13.1	11.8	7.2	
$(C_5Me_4Et)_3Sm$[9]										
ring 1	0.51	0.37	0.33	0.18		19.5	14.2	12.8	6.9	
ring 2	0.50	0.41	0.35	0.24		19.4	16.5	13.5	9.4	
ring 3	0.49	0.36	0.33	0.17		19.2	13.7	12.5	6.4	
$(C_5Me_4{}^iPr)_3La$[7]										
ring 1	0.50	0.35	0.31	0.19		19.2	13.3	12.0	7.2	
ring 2	0.49	0.34	0.32	0.15		19.0	13.0	12.2	5.9	
ring 3	0.48	0.32	0.31	0.19		18.6	12.0	12.3	7.1	
$(C_5Me_5)_2Sm(PC_4H_2{}^tBu_2)$[17]										
ring 1	0.50	0.38	0.36	0.20	0.13	19.5	14.7	13.9	7.5	5.0
ring 2	0.39	0.33	0.31	0.19	0.16	15.0	12.8	11.9	7.1	6.1
$(C_5Me_4Et)_3La$[7]										
ring 1	0.48	0.34	0.29	0.25		18.6	18.5	11.1	9.4	
ring 2	0.48	0.31	0.31	0.20		18.6	12.1	11.9	7.5	
ring 3	0.46	0.32	0.28	0.21		17.9	12.4	10.6	7.9	
$[(C_5Me_5)_2U]_2(C_6H_6)$[16]										
ring 1	0.48	0.36	0.24	0.07	0.06	18.5	14.2	9.3	2.7	2.2
ring 2	0.45	0.43	0.22	0.14	0.12	17.5	16.7	8.2	5.2	4.7
ring 3	0.44	0.40	0.18	0.13	0.04	17.3	15.7	6.6	4.9	1.6
ring 4	0.41	0.36	0.24	0.18	0.12	15.8	14.0	9.3	7.1	4.7
$[(C_5Me_5)_2SmCl]_3$[24]										
ring 1	0.42	0.21	0.19	0.11	0.09	15.2	7.8	7.2	4.1	3.4
ring 2	0.35	0.17	0.14	0.12	0.10	12.7	6.4	5.2	4.4	3.9
ring 3	0.30	0.19	0.12	0.11	−0.01	11.6	7.2	4.5	4.1	−0.2
$[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$[25]										
ring 1	0.41	0.37	0.21	0.13	0.07	16.1	14.1	8.1	4.9	2.7
$[(C_5Me_5)_2Sm]_2(CH_2CHPh)$[26]										
ring 1	0.41	0.28	0.20	0.19	0.15	15.7	10.6	7.8	7.3	5.9
ring 2	0.40	0.28	0.26	0.11	0.09	15.2	10.7	10.0	4.2	3.4
ring 3	0.29	0.22	0.14	0.14	0.09	11.1	8.5	5.5	5.3	3.4
ring 4	0.25	0.24	0.21	0.03	−0.07	9.6	8.9	8.2	1.2	−2.7
$(C_5Me_5)_2Sm(C_5H_5)$[18]										
ring 1	0.41	0.25	0.24	0.14	0.11	15.6	9.4	9.1	5.3	3.9
ring 2	0.36	0.34	0.26	0.12	0.05	13.6	12.6	9.8	4.6	2.0
$[Me_2Si(C_5Me_4)_2]Sm(C_5Me_5)$[19]										
ring 1	0.40	0.39	0.25	0.18	0.03	15.2	15.2	9.7	7.0	1.3
ring 2	0.36	0.28	0.24	0.09		13.7	10.6	9.0	3.4	
ring 3	0.34	0.31	0.09	0.09		12.9	11.8	3.6	3.3	
$(C_5Me_5)_2Sm(P_3C_2{}^tBu_2)(THF)$[27]										
ring 1	0.37	0.22	0.20	0.13	0.13	14.4	8.3	7.7	5.2	4.9
ring 2	0.24	0.22	0.20	0.17	0.15	9.4	8.3	7.7	6.2	5.7
$(C_5Me_4H)_3Sm$[20,21]										
ring 1	0.35	0.34	0.12	0.06		13.5	13.4	4.4	2.0	
$(C_5Me_5)_2Sm(CH_2CHCHPh)(OC_8H_8)$[28]										
ring 1	0.35	0.25	0.25	0.21	0.15	13.6	9.7	9.5	8.0	5.6
ring 2	0.30	0.29	0.21	0.20	0.17	11.4	11.1	8.0	7.6	6.6
$[(C_5Me_5)_2U]_2(\mu\text{-}O)$[29]										
ring 1	0.35	0.14	0.14	0.13	0.05	13.5	5.5	5.4	5.1	2.1
ring 2	0.29	0.17	0.12	0.10	0.02	11.2	6.5	4.8	3.7	0.8
ring 3	0.28	0.15	0.12	0.07	−0.002	10.5	5.6	4.5	2.6	−0.1
ring 4	0.18	0.16	0.13	0.08	0.06	6.9	6.1	5.0	2.9	2.5
$(C_5Me_5)_2Sm(AsPh_2)$[30]										
ring1	0.34	0.19	0.18	0.14	0.05	12.8	7.2	7.1	5.5	2.1
ring 2	0.33	0.22	0.18	0.11	0.06	12.1	8.1	6.9	4.5	2.2
ring 3	0.30	0.20	0.17	0.11	−0.01	11.2	7.9	6.6	4.0	−0.3
ring 4	0.28	0.20	0.17	0.10	0.08	10.4	7.6	6.4	3.6	3.2
$(C_5Me_5)_2Sm[N(SiMe_3)_2]$[31]										
ring 1	0.33	0.24	0.21	0.17	0.17	12.8	9.0	7.9	6.5	6.5
ring 2	0.26	0.25	0.18	0.17	0.15	9.9	9.7	6.9	6.5	5.7

Table 2. Continued

compound	C(a)	C(b)	C(c)	C(d)	C(e)	θ[C(a)]	θ[C(b)]	θ[C(c)]	θ[C(d)]	θ[C(e)]
$(C_5Me_4Et)_2Sm[CH(SiMe_3)_2]$[32]										
ring 1	0.33	0.24	0.11	0.08		12.7	9.1	4.4	3.2	
ring 2	0.24	0.20	0.16	0.14		9.0	7.7	6.2	5.5	
$(C_5Me_5)_2Sm[(NSiMe_3)(CPh)N{=}CHPh]$[33]										
ring 1	0.33	0.24	0.20	0.18	0.15	12.8	9.0	7.6	7.1	5.6
ring 2	0.19	0.19	0.16	0.14	0.11	7.4	7.1	6.0	5.5	4.3
$(C_5Me_5)_2UH(DMPE)$[34]										
ring 1	0.32	0.28	0.18	0.17	0.07	11.8	9.7	6.9	6.6	2.4
ring 2	0.31	0.26	0.20	0.12	0.11	11.7	9.7	7.2	4.4	4.2
$[(C_5Me_5)_2Sm]_2(C_{14}H_{10})$[35]										
ring 1	0.32	0.23	0.15	0.11	0.03	12.4	8.6	5.8	4.3	1.2
ring 2	0.29	0.22	0.15	0.14	0.11	11.0	8.6	5.8	5.2	4.1
$[(C_5Me_5)_2Sm]_2[(PhN)OC]_2$[36,37]										
ring 1	0.29	0.16	0.14	0.12	0.06	10.6	6.1	5.0	4.6	2.4
$(C_5Me_5)_2U[N(SiMe_3)_2]$[38]										
ring 1	0.29	0.25	0.20	0.17	0.17	11.1	9.4	7.6	6.5	6.5
ring 2	0.26	0.24	0.18	0.18	0.13	10.1	9.0	6.9	6.7	5.1
$(C_5Me_5)_2Nd[CH(SiMe_3)_2]$[39,40]										
ring 1	0.28	0.20	0.19	0.15	0.01	10.7	7.7	7.4	5.4	0.5
ring 2	0.26	0.16	0.13	0.09	0.05	9.6	6.8	5.0	3.4	1.9
$[(C_5Me_5)_2Sm]_2(C_{13}H_9N)_2$[35]										
ring 1	0.28	0.23	0.15	0.14	0.13	10.8	8.6	5.6	5.2	4.9
ring 2	0.25	0.17	0.15	0.08	0.07	9.4	6.5	5.9	2.9	2.8
$(C_5Me_5)_2Sm(CH_2CHCH_2)$[28]										
ring 1	0.28	0.20	0.13	0.13	0.05	10.5	7.5	4.9	4.7	1.9
ring 2	0.23	0.17	0.17	0.09	0.08	8.8	6.6	6.5	3.6	3.2
$(C_5Me_5)_2Ce[CH(SiMe_3)_2]$[41]										
ring 1	0.28	0.20	0.15	0.07	0.06	11.0	7.6	5.8	2.8	2.3
ring 2	0.18	0.17	0.16	0.14	0.13	7.0	6.8	5.9	5.1	5.0
$(C_5Me_5)_2Sm(OC_6H_2{}^tBu_3)$[42]										
ring 1	0.27	0.25	0.25	0.19	0.09	10.0	9.8	9.4	6.9	3.5
$(C_5Me_5)_2SmCl_2Li(OEt_2)_2$[43]										
ring 1	0.26	0.12	0.06			9.9	4.6	2.4		
$\{[(Me_3Si)_2N](C_5Me_5)U\}_2(C_6H_6)$[16]										
ring 1	0.26	0.22	0.20	0.12	0.08	9.8	8.3	7.5	4.4	3.0
$[(C_5Me_4{}^iPr)_2Sm]_2(\mu\text{-}O)$[44]										
ring 1	0.25	0.12	0.05	0.04		9.7	4.6	2.1	1.7	
ring 2	0.22	0.20	0.14	0.10		8.3	7.6	5.5	3.7	
ring 3	0.20	0.18	0.10	0.05		7.6	6.9	4.0	2.0	
ring 4	0.20	0.19	0.11	0.09		7.4	7.4	4.1	3.3	
$(C_5Me_5)_2Eu$[48]										
ring 1	0.24	0.15	0.10	0.08	0.07	9.1	5.7	3.7	3.2	2.6
ring 2	0.20	0.16	0.15	0.12	0.04	7.4	6.2	5.8	4.4	1.6
$(C_5Me_5)_2Sm$[47,48]										
ring 1	0.24	0.16	0.10	0.08	0.08	9.0	6.1	3.6	3.1	3.0
ring 2	0.19	0.17	0.14	0.12	0.05	7.1	6.5	5.3	4.5	2.0
$(C_5Me_4H)_3U$[22,23]										
ring 1	0.23	0.22	0.09	0.07		8.8	8.6	3.5	2.8	
$[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$[45]										
ring 1	0.22	0.11	−0.01			8.6	4.1	−0.2		
$(C_5Me_5)_2Yb$[49]										
ring 1	0.22	0.16	0.14	0.07	0.03	8.3	5.9	5.4	2.8	1.1
ring 2	0.18	0.16	0.14	0.13	0.08	6.9	6.1	5.4	5.0	3.2
$(C_5Me_4H)_3La$[20,21]										
ring 1	0.19	0.19	0.10	0.08		7.4	7.4	3.6	2.9	
$[(C_5Me_5)_2Nd]_2(\mu\text{-}O)$[46]										
ring 1	0.13	0.09	0.03			5.0	3.5	1.3		
$[(C_5Me_5)_2La]_2(\mu\text{-}O)$[44]										
ring 1	0.12	0.08	−0.01			4.4	3.0	−0.4		

[a] The a−e labels are used to correlate methyl displacements with θ angles within each ring. Compounds are listed in order of decreasing maximum out-of-plane displacement. When these are equal, the order is determined by decreasing values of the other rings, and if equal, by decreasing maximum θ values.

Table 3. Maximum and Minimum Out-of-Plane Methyl Displacements (Å) from the Average Ring Carbon Plane Generated by the $(C_5Me_4R)^{1-}$ Ligands and the (average ring carbon plane)−C(ring)−C(Me) Angles, θ (deg), for the Compounds in Figure 2 Listed in Decreasing Order of the Maximum Displacement[a]

	displacement range			θ range	
compound	high	median	low	high	low
$(C_5Me_5)_3UCl^{10}$	0.54	0.36	0.20	20.9	7.8
$(C_5Me_5)_3UF^{10}$	0.54	0.34	0.16	20.8	6.4
$[C_5Me_4(SiMe_3)]_3La^7$	0.54	0.33	0.19	21.1	7.2
$(C_5Me_5)_3U(CO)^{13}$	0.53	0.34	0.25	20.8	9.7
$(C_5Me_5)_3U(N_2)^{14}$	0.53	0.34	0.24	20.7	9.4
$(C_5Me_5)_3Sm^1$	0.52	0.36	0.18	20.3	6.7
$(C_5Me_5)_3UMe^{11}$	0.52	0.35	0.21	20.2	8.1
$(C_5Me_5)_3Nd^6$	0.52	0.34	0.17	20.2	6.6
$(C_5Me_5)_3Pr^8$	0.52	0.33	0.17	20.0	6.4
$(C_5Me_5)_3U^5$	0.52	0.34	0.18	19.9	6.8
$(C_5Me_5)_3ThH^{12}$	0.51	0.31	0.20	19.8	7.6
$(C_5Me_4Et)_3Sm^9$	0.51	0.36	0.17	19.5	6.4
$(C_5Me_5)_3Ce^8$	0.50	0.32	0.17	19.5	6.4
$(C_5Me_5)_3La^7$	0.50	0.31	0.16	19.4	6.1
$(C_5Me_4{}^iPr)_3La^7$	0.50	0.32	0.15	19.2	5.9
$(C_5Me_5)_2Sm(PC_4H_2{}^tBu_2)^{17}$	0.50	0.32	0.13	19.5	5.0
$(C_5Me_4Et)_3La^7$	0.48	0.31	0.20	18.6	7.5
$[(C_5Me_5)_2U]_2(C_6H_6)^{16}$	0.48	0.23	0.04	18.5	1.6
$[(C_5Me_5)_2SmCl]_3{}^{24}$	0.42	0.14	−0.01	15.2	−0.2
$[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)^{25}$	0.41	0.21	0.07	16.1	2.7
$[(C_5Me_5)_2Sm]_2(CH_2CHPh)^{26}$	0.41	0.21	−0.07	15.7	−2.7
$(C_5Me_5)_2Sm(C_5H_5)^{18}$	0.41	0.25	0.05	15.6	2.0
$[Me_2Si(C_5Me_4)_2]Sm(C_5Me_5)^{19}$	0.40	0.25	0.03	15.2	1.3
$(C_5Me_5)_2Sm(P_3C_2{}^tBu_2)(THF)^{27}$	0.37	0.20	0.13	14.4	4.9
$(C_5Me_4H)_3Sm^{20,21}$	0.35	0.23	0.06	13.5	2.0
$(C_5Me_5)_2Sm(CH_2CHCHPh)(OC_8H_8)^{28}$	0.35	0.23	0.15	13.6	5.6
$[(C_5Me_5)_2U]_2(\mu\text{-}O)^{29}$	0.35	0.13	−0.002	13.5	−0.1
$(C_5Me)_2Sm(AsPh_2)^{30}$	0.34	0.18	−0.01	12.8	−0.3
$(C_5Me_5)_2Sm[N(SiMe_3)_2]^{31}$	0.33	0.19	0.15	12.8	5.7
$(C_5Me_4Et)_2Sm[CH(SiMe_3)_2]^{32}$	0.33	0.18	0.08	12.7	3.2
$(C_5Me_5)_2Sm\overline{[(NSiMe_3)(CPh)N}{=}CHPh]^{33}$	0.33	0.19	0.11	12.8	4.3
$(C_5Me_5)_2UH(DMPE)^{34}$	0.32	0.19	0.07	11.8	2.4
$[(C_5Me_5)_2Sm]_2(C_{14}H_{10})^{35}$	0.32	0.15	0.03	12.4	1.2
$[(C_5Me_5)_2Sm]_2[(PhN)OC]_2{}^{36,37}$	0.29	0.14	0.06	10.6	2.4
$(C_5Me_5)_2U[N(SiMe_3)_2]^{38}$	0.29	0.19	0.13	11.1	5.1
$(C_5Me_5)_2Nd[CH(SiMe_3)_2]^{39,40}$	0.28	0.16	0.01	10.7	0.5
$[(C_5Me_5)_2Sm]_2(C_{13}H_9N)_2{}^{35}$	0.28	0.15	0.07	10.8	2.8
$(C_5Me_5)_2Sm(CH_2CHCH_2)^{28}$	0.28	0.15	0.05	10.5	1.9
$(C_5Me_5)_2Ce[CH(SiMe_3)_2]^{41}$	0.28	0.16	0.06	11.0	2.3
$(C_5Me_5)_2Sm(OC_6H_2{}^tBu_3)^{42}$	0.27	0.25	0.09	10.1	3.5
$(C_5Me_5)_2SmCl_2Li(OEt_2)_2{}^{43}$	0.26	0.12	0.06	9.9	2.4
$\{[(Me_3Si)_2N](C_5Me_5)U\}_2(C_6H_6)^{16}$	0.26	0.20	0.08	9.8	3.0
$[(C_5Me_4{}^iPr)_2Sm]_2(\mu\text{-}O)^{44}$	0.25	0.13	0.04	0.7	1.7
$(C_5Me_5)_2Eu^{48}$	0.24	0.14	0.04	9.1	1.6
$(C_5Me_5)_2Sm^{47,48}$	0.24	0.13	0.05	9.0	2.0
$(C_5Me_4H)_3U^{22,23}$	0.23	0.16	0.07	8.8	2.8
$[(C_5Me_5)_2Sm]_2(\mu\text{-}O)^{45}$	0.22	0.11	−0.01	8.6	−0.2
$(C_5Me_5)_2Yb^{49}$	0.22	0.14	0.03	8.3	1.1
$(C_5Me_4H)_3La^{20,21}$	0.19	0.15	0.08	7.4	2.9
$[(C_5Me_5)_2Nd]_2(\mu\text{-}O)^{46}$	0.13	0.09	0.03	5.0	1.3
$[(C_5Me_5)_2La]_2(\mu\text{-}O)^{44}$	0.12	0.08	−0.01	4.4	−0.4

[a] When these are equal, the order is determined by decreasing values of the other rings, and if equal, by decreasing maximum θ values.

the reactivity of $(C_5Me_5)_2Sm(PC_4H_2{}^tBu_2)$,[17] remains to be determined. The less sterically crowded $(C_5Me_4R)^{1-}$ complexes in Table 2 include compounds that are closely related to the $(C_5Me_5)_3M$ complexes, namely $(C_5Me_5)_2Sm(C_5H_5)$,[18] $[Me_2Si(C_5Me_4)_2]Sm(C_5Me_5)$,[19] and $(C_5Me_4H)_3M$ (M = La,[20,21] Sm,[20,21] U,[22,23]). Also included in Table 2 are compounds that represent common types of f-element $(C_5Me_4R)^{1-}$ complexes in the literature, as well as complexes that contain extremes in coordination number and long individual M−C(C_5Me_4R) distances, but that still display normal $(C_5Me_4R)^{1-}$ reactivity.[16,24−49] Samarium and uranium complexes were primarily chosen since they constitute the most common examples in the lanthanide and actinide series, respectively.

Trends in the Data

$(C_5Me_5)_3M$ Complexes. In all of the $(C_5Me_5)_3M$ complexes, the largest out-of-plane displacement corresponds to methyl group C(4) bound to the C(1) ring carbon that has the longest M−C(ring) bond distance, Table 1 and Figure 3. However, the methyl group with the smallest displacement, C(5), is bound to the C(2) ring carbon that has an intermediate M−C(ring) bond distance. Hence, no simple correlation between out-of-plane methyl displacement and M−C(C_5Me_5) distance predicts the methyl displacements for C(5) and C(6).

There does, however, appear to be a correlation between the out-of-plane methyl displacements with the extent to which the ring carbon is out of the trigonal plane defined by the metal and the three ring centroids, Figure 3. C(1) is in this plane and has the longest M−C bond distance, as well as the largest methyl displacement; it is the most-crowded C−Me unit in these molecules. In $(C_5Me_5)_3Sm$, this methyl displacement is 0.52 Å. Of the compounds in Table 1, the next largest out-of-plane displacement observed is for C(6), whose ring centroid−C(3)−C(6) vector forms a 37.5° angle with the trigonal plane of the metal and the three ring centroids. For $(C_5Me_5)_3Sm$, this displacement is 0.36 Å. The ring centroid−C(2)−C(5) vector forms a 72.9° angle with the trigonal plane of the molecule, and consequently, C(5) is in the least-congested area of the molecule. Hence, C(5) has the smallest methyl displacement, 0.18 Å in $(C_5Me_5)_3Sm$.

The structural data in Tables 1 and 2 allow the out-of-plane methyl displacements to be analyzed as a function of ionic radius for similar compounds and the trends in the data can be readily compared in Figure 2. This figure is constructed in the order of decreasing maximum methyl displacements, which are represented by triangles. Of the sterically crowded $(C_5Me_5)_3M$ complexes, the maximum methyl displacements are in the narrow range of 0.50−0.52 Å, but there is a regular decrease in θ as a function of increasing metal size: $(C_5Me_5)_3Sm$,[1] $(C_5Me_5)_3Nd$,[6] $(C_5Me_5)_3Pr$,[8] $(C_5Me_5)_3U$,[5] $(C_5Me_5)_3Ce$,[8] and $(C_5Me_5)_3La$.[7] This is consistent with decreasing steric crowding for complexes of larger metal ions.

In contrast to the regularity in maximum displacements, the minimum and median values do not always parallel the maximum displacement values. Overall, the maximum, median, and minimum displacements for the $(C_5Me_5)_3M$ series fall into three distinct ranges: 0.54−0.50, 0.36−0.30, and 0.25−0.16 Å, respectively.

$(C_5Me_5)_3UX$ and $(C_5Me_5)_3UL$. Table 1 also presents data for tris(pentamethylcyclopentadienyl) complexes that contain one additional ligand. The trivalent complexes $(C_5Me_5)_3U(CO)$[13] and $(C_5Me_5)_3U(N_2)$[14] have maximum and intermediate out-of-plane displacement values that are all numerically larger than those of $(C_5Me_5)_3U$, but the 0.01−0.02 Å differences are small and may be within the error limits. Only for the minimum displacement values involving the C(5) methyl, which is oriented toward the fourth ligand as shown

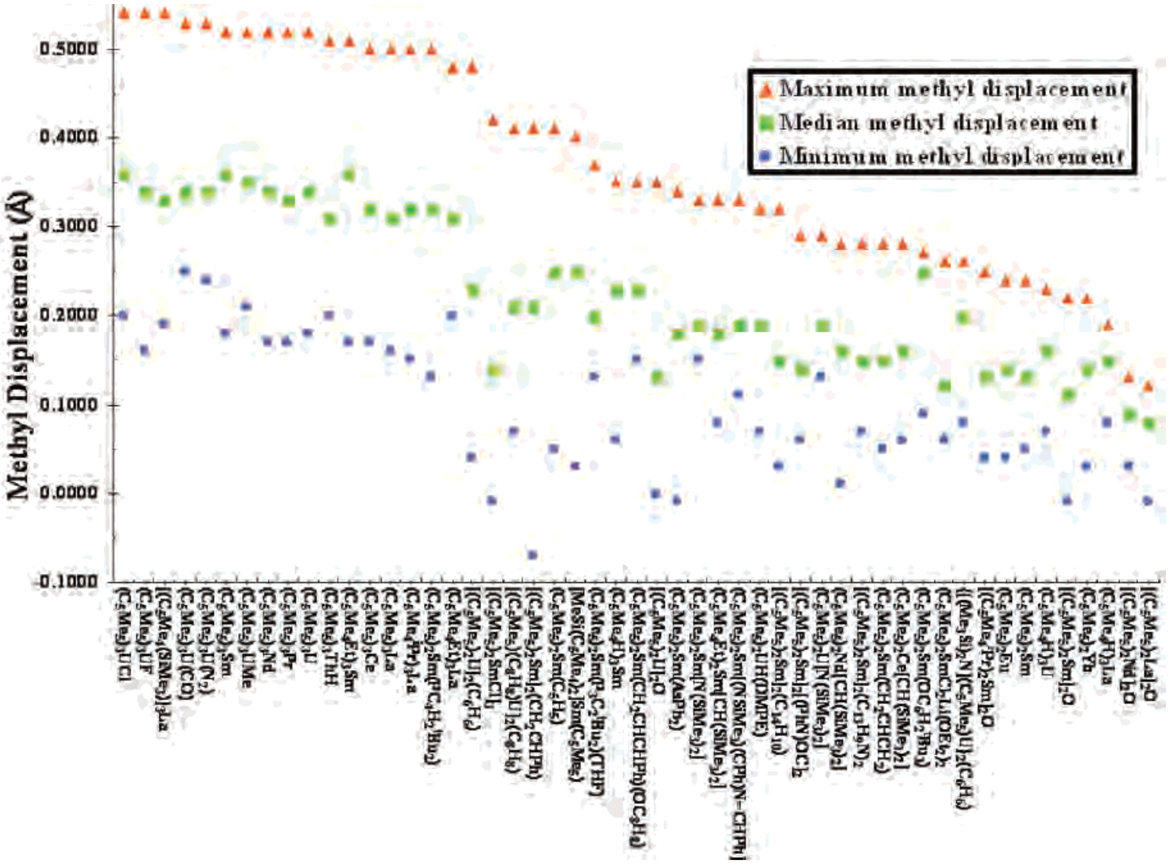
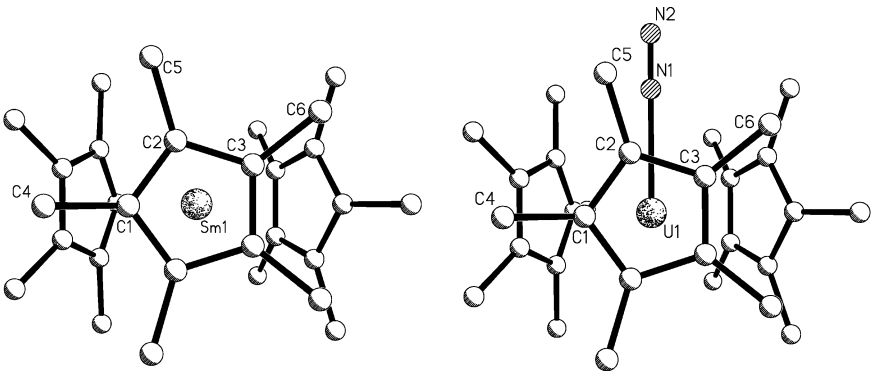


Figure 2. The maximum (triangles), median (squares), and minimum (circles) out-of-plane methyl displacements (Å) for the complexes in Tables 1−3 shown in order of decreasing maximum methyl displacement.



(a)

(b)

Figure 3. Ball and stick representations of tris(pentamethylcyclopentadienyl) complexes with unique atoms labeled: (a) $(C_5Me_5)_3Sm$ and (b) $(C_5Me_5)_3U(N_2)$, the disordered portion of the N_2 ligand is omitted. The diagrams are oriented so the plane of the metal and the three ring centroids is horizontal.

in Figure 3, do the $(C_5Me_5)_3UL$ complexes have displacements that are 0.06−0.07 Å greater than those in $(C_5Me_5)_3U$.

The tetravalent $(C_5Me_5)_3UX$ complexes (X = Cl,[10] F,[10] Me[11]) would also be expected to have larger displacements than $(C_5Me_5)_3U$ since they have a fourth ligand and involve smaller U(IV) ions.[57] As expected these complexes do have larger maximum and intermediate displacements. The minimum displacements for $(C_5Me_5)_3UCl$ and $(C_5Me_5)_3UMe$ are also larger than those in $(C_5Me_5)_3U$, but for $(C_5Me_5)_3UF$,[10] this C(5) displacement is numerically smaller than the minimum displacement in $(C_5Me_5)_3U$.

$(C_5Me_5)_3ThH$. The only thorium complex in the list, $(C_5Me_5)_3ThH$,[12] is anomalous in that it has the extreme structural parameters of the other 16 compounds containing three $(C_5Me_4R)^{1-}$ rings, but it has not yet been observed to display unusual $(C_5Me_5)^{1-}$ ring reactivity. More data are needed before the reasons for this exception are understood.

$(C_5Me_4R)_3M$ Complexes. For these less symmetric complexes, the range of maximum displacements per ring ranges from 0.54 to 0.48 Å. This range is slightly wider than the analogous displacements in the $(C_5Me_5)_3M$, $(C_5Me_5)_3ML$, and $(C_5Me_5)_3MX$ complexes. Although there are only two structurally characterized $(C_5Me_4R)_3Ln$ complexes that allow

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[57] Shannon, R. D. *Acta Crystallogr. A* **1976**, *23*, 751.

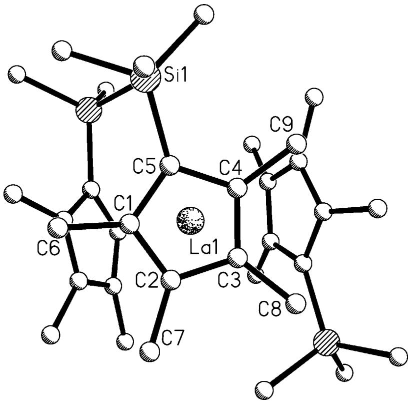


Figure 4. Ball and stick representations of $[C_5Me_4(SiMe_3)]_3La$ showing the $SiMe_3$ groups oriented out of the plane of the metal and the three ring centroids.

a comparison based on metal size, $(C_5Me_4Et)_3La$ and $(C_5Me_4Et)_3Sm$ show the same trend observed for the $(C_5Me_5)_3Ln$ complexes: θ values decrease as metal size increases.

The $[C_5Me_4(SiMe_3)]_3La$,[7] $(C_5Me_4{}^iPr)_3La$,[7] and $(C_5Me_4Et)_3La$[7] series has maximum methyl displacement values that decrease as the size of the non-methyl ring substituent decreases. However, $(C_5Me_5)_3La$[7] has a greater maximum displacement than either $(C_5Me_4{}^iPr)_3La$ or $(C_5Me_4Et)_3La$. This demonstrates that with the less-symmetrical complexes, distortions can occur that evidently alter the maximum displacement of the methyl groups relative to complexes that have five identical groups.

With the $(C_5Me_4R)_3M$ complexes, the out-of-plane displacement of the carbon or silicon atom of the R substituent can also be evaluated. The R groups in all of these complexes are located at a position away from the most-congested area of the complex, as shown in Figure 4, in a position similar to C(5) in Figure 3. For $[C_5Me_4(SiMe_3)]_3La$,[7] the three silicon out-of-plane displacements are irregular: 0.50, 0.20, and 0.16 Å. None of these are numerically as large as the 0.54 Å maximum methyl displacement observed in this complex. The 0.16 Å minimum silicon displacement is smaller than the minimum methyl displacement in this complex. The other $(C_5Me_4R)_3M$ complexes also have a large range of R-displacements, and none are as extreme as the maximum methyl displacement in the respective complex. These are 0.17, 0.15, and 0.11 Å for the methine carbons of the isopropyl group in $(C_5Me_4{}^iPr)_3La$, 0.25, 0.05, and 0.03 Å for the methylene carbons of the ethyl group in $(C_5Me_4Et)_3La$,[7] and 0.25, 0.08, and 0.11 Å for the analogous carbons in $(C_5Me_4Et)_3Sm$.[9] These data show no correlation between the size of the nonmethyl substituent and its out-of-plane displacement.

$(C_5Me_4R)_3M$ Complexes With Normal M−C(C_5Me_4R) Distances and Normal $(C_5Me_4R)^{1-}$ Reaction Chemistry. After the 18th entry in Figure 2, $(C_5Me_4Et)_3La$, there is a drop in the value of the *maximum* methyl displacements. All of the entries from this point on, 33 examples in all, have normal metal−ring carbon distances and normal cyclopentadienyl ring reactivity, i.e., the rings serve as unreactive ancillary ligands. The rings have not been observed to react as η^1-alkyls or as reducing agents as in the sterically crowded complexes.[3,8,15]

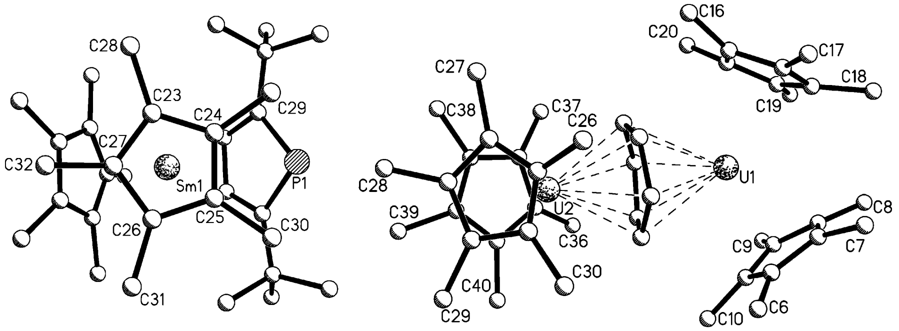
Hence, Figure 2 shows a surprisingly distinct demarcation on the basis of maximum displacement values between the sterically crowded tris(pentamethylcyclopentadienyl) complexes with high cyclopentadienyl reactivity and complexes that display conventional cyclopentadienyl behavior. As opposed to the 0.48−0.54 Å range of maximum displacement values found for the sterically crowded entries in Figure 2, the maximum displacement values for the last 33 entries vary from 0.12 to 0.42 Å. The median and minimum values of these complexes have ranges of 0.8−0.25 and −0.7−0.15 Å, respectively, and show no obvious trends based on steric crowding. Since the last 33 complexes analyzed are not comprehensive, but rather representative, these ranges may actually be wider. However, the data are sufficient to show trends.

The largest maximum displacements for the sterically "normal" complexes are the 0.42, 0.41, 0.41, and 0.41 Å values for $[(C_5Me_5)_2SmCl]_3$,[24] $[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$,[25] $[(C_5Me_5)_2Sm]_2(CH_2CHPh)$,[26] and $(C_5Me_5)_2Sm(C_5H_5)$,[18] respectively. As in the $(C_5Me_5)_3M$ complexes, the out-of-plane displacement is typically largest for the methyl group that is oriented directly toward two methyl substituents of an adjacent ring. These complexes define an upper limit for maximum displacement with normal cyclopentadienyl ring reactivity.

The correlation of decreasing maximum out-of-plane displacement with increasing metal size, as observed with the sterically crowded complexes, is found with two series of compounds among the last 33 complexes in Figure 2. This occurs for the $(C_5Me_4H)_3M$ (M = Sm,[20,21] U,[22,23] La[20,21]) and $(C_5Me_5)_2M[N(SiMe_3)_2]$ (M = Sm,[31] U[38]) compounds. For the $[(C_5Me_4R)_2Ln]_2(\mu\text{-}O)$ (Ln = Sm,[44,45] Nd,[46] La[44]) complexes, the methyl displacements also decrease with increasing metal radius, but the $[(C_5Me_5)_2U]_2(\mu\text{-}O)$[29] analogue has a much large displacement, 0.35 Å, than that of $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$, 0.22 Å. This is inconsistent with the relative ionic radii.[57]

Interestingly, for the formally lowest coordinate systems in this compilation, the series of $(C_5Me_5)_2M$ bent metallocenes (M = Sm,[47,48] Eu,[48] Yb[49]), a reverse trend in terms of methyl displacement versus ionic radius is observed. Although the 0.02 Å range of methyl displacements is small in this case, the smaller metal, Yb, has a smaller out-of-plane displacement, 0.22 Å, than that of the larger metals, Sm and Eu, which have 0.24 Å maximum displacements. The $(C_5Me_5)_2M$ complexes were included to show that even in these sterically unsaturated complexes, the methyl groups do not reside completely in the cyclopentadienyl plane. The maximum out-of-plane displacements for these complexes are equivalent to some of the minimum displacements for the sterically crowded complexes. This means that some of the displacements in sterically crowded complexes are no larger than those found in these sterically unsaturated species.

Bis(pentamethylcyclopentadienyl) f-Element Complexes with Large Maximum Displacements. Among the first 18 entries in Figure 2 that have high values of maximum



(a) **(b)**

Figure 5. Ball and stick representations of bis(pentamethylcyclopentadienyl) complexes that have large maximum out-of-plane methyl displacements (a) $(C_5Me_5)_2Sm(PC_4H_2{}^tBu_2)$ and (b) $[(C_5Me_5)_2U]_2(C_6H_6)$.

displacements, there are only two bis(pentamethylcyclopentadienyl) f-element complexes, $[(C_5Me_5)_2U]_2(C_6H_6)$[16] and $(C_5Me_5)_2Sm(PC_4H_2{}^tBu_2)$,[17] Figure 5. All the rest have three cyclopentadienyl rings. The reactivity of these two complexes is of interest since they have maximum displacements of the type found with the other 16 entries that have long M−C(C_5Me_5) distances and unusual $(C_5Me_5)^{1-}$ reactivity (with the exception of $(C_5Me_5)_3ThH$).[12]

$[(C_5Me_5)_2U]_2(C_6H_6)$ has been shown to have unusual cyclopentadienyl chemistry including sterically induced reduction reactivity and $(C_5Me_5)^{1-}$ substitution chemistry.[16] It clearly fits in with the other sterically crowded examples in terms of reactivity.

The reaction chemistry of $(C_5Me_5)_2Sm(PC_4H_2{}^tBu_2)$[17] has not yet been reported. $(C_5Me_5)_2Sm(PC_4H_2{}^tBu_2)$[17] is unusual in that the two $(C_5Me_5)^{1-}$ rings have very different maximum displacements. C(32) is the methyl group with the largest displacement, 0.50 Å, and is in an analogous position to C(4) for the $(C_5Me_5)_3M$ complexes in Figure 3. The 0.39 Å maximum methyl displacement of the other $(C_5Me_5)^{1-}$ ligand in $(C_5Me_5)_2Sm(PC_4H_2{}^tBu_2)$[17] is more similar to those of the last 33 entries in Figure 2. Hence, this complex appears to be on the borderline since one ring has parameters consistent with steric crowding while the other does not. In addition, the facile η^5-to-η^1 conversion available to the $(PC_4H_2{}^tBu_2)^{1-}$ ligand might also complicate the structure/reactivity correlation by relieving steric crowding and decreasing $(C_5Me_5)^{1-}$ reactivity.

Discussion

The data collected here suggest several generalizations that can be evaluated in the future as more structural data are obtained on both sterically crowded and conventional cyclopentadienyl f-element complexes. First, methyl group displacements from the cyclopentadienyl rings in f-element complexes occur not only for sterically crowded complexes such as the $(C_5Me_5)_3M$, $(C_5Me_5)_3ML$, and $(C_5Me_5)_3MX$ series but also for bis(pentamethylcyclopentadienyl) complexes and even the sterically unsaturated series, $(C_5Me_5)_2M$. Out-of-plane methyl displacement is normal for all of these complexes.

Second, the amount of displacement can vary considerably from one methyl to another within a complex such that sterically unsaturated complexes can have some displacements larger than those in sterically crowded complexes. There is a wide range in the values of out-of-plane displacements even within a complex.

Third, the most useful comparative displacement value appears to be the maximum methyl displacement. Using this parameter, there is a clear demarcation between the sterically crowded complexes that have unusual cyclopentadienyl chemistry and conventional complexes in which the cyclopentadienyl rings are not reactive. With the data presently available, a maximum methyl displacement of 0.48 Å or higher suggests cyclopentadienyl ring reactivity and a value of 0.42 Å and below suggests normal cyclopentadienyl ring behavior. Time will tell if these limits will continue to be predictive. Given the wide variation observed in individual displacement values, as well as M−C(ring) bond distances within a complex, it seems quite possible that some unusual complexes may have displacement values that will not fit into these limits exactly. Nonetheless, the assembled data suggest quite strongly that there is a general trend that cyclopentadienyl ring reactivity is associated with a maximum methyl displacement of 0.48 Å or higher. As with most generalizations, a useful feature is that attention gets directed to the exceptions. $(C_5Me_5)_3ThH$ is the only exception known so far to this generalization, and clearly, this and related complexes deserve more study.

Fourth, within a series of sterically crowded complexes, a rationale based on steric factors seems to explain the trends in maximum methyl displacement values. Hence, the largest displacement is found for the most-crowded methyl group in the trigonal plane of the complex. Methyl displacements decrease as the size of the metal increases and the steric crowding decreases. Addition of a fourth ligand to a $(C_5Me_5)_3M$ complex increases steric crowding.

Fifth, it appears that maximum displacements cannot be regularly predicted for $(C_5Me_4R)_3M$ complexes since the reduced symmetry can lead to unexpectedly high and low methyl displacements. In this regard, the data reinforce the importance of generating sterically crowded complexes with high-symmetry ligands. Simply replacing a methyl group in a $(C_5Me_5)^{1-}$ complex with a larger substituent does not necessarily increase the maximum displacement value or the reactivity.[7,9]

Conclusion

Methyl groups are displaced out of the plane of the cyclopentadienyl rings in $(C_5Me_5)^{1-}$ and $(C_5Me_4R)^{1-}$ f-element complexes regardless of whether the complex is sterically crowded, sterically unsaturated, or sterically conventional. Moreover, a large range of methyl displacements is typically found within a single complex. Despite the diversity of the data, it appears that the maximum out-of-plane methyl displacement measurements offer a useful parameter to evaluate steric crowding and predict unusual cyclopentadienyl reactivity. Hence, with the data presently in hand, methyl displacements greater than or equal to 0.48 Å are observed in sterically crowded complexes with long $M-C(C_5R_5)$ bond distances, small (C_5R_5 ring centroid)$-M-$(C_5R_5 ring centroid) angles, and reactive $(C_5R_5)^{1-}$ rings, while complexes with conventional $M-C(C_5R_5)$ bond distances and angles and no unusual ring reactivity have maximum out-of-plane methyl displacements less than or equal to 0.42 Å. This generalization will likely require some modification as more data are collected.

Acknowledgment. We thank the National Science Foundation for support of this research.

IC051130H