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Synthesis and Structure of Tris(alkyl- and silyl-tetramethylcyclopentadienyl) Complexes of Lanthanum

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In efforts to make sterically crowded tris(peralkylcyclopentadienyl) complexes of lanthanum for the exploration of sterically induced reduction chemistry with a diamagnetic system, the synthesis of $(C_5Me_4R)_3La$ complexes has been pursued with R = Me, Et, ^{i}Pr, and $SiMe_3$. The complexes were synthesized in four steps: reaction of $LaCl_3$ with KC_5Me_4R to form $(C_5Me_4R)_2LaCl_2K(THF)_2$, addition of allylmagnesium chloride to make $(C_5Me_4R)_2La(C_3H_5)$, protonolysis with Et_3NHBPh_4 to make $[(C_5Me_4R)_2La][BPh_4]$, and finally the replacement of BPh_4^- with $C_5Me_4R^-$ using KC_5Me_4R to make $(C_5Me_4R)_3La$. X-ray crystallographic data were obtainable on the $(C_5Me_4R)_3La$ complexes for R = Me, Et, ^{i}Pr, and $SiMe_3$. In each complex, the three C_5Me_4R ring centroids define a trigonal planar geometry around La. The average La−(ring centroid) distances are 2.64, 2.65, 2.66, and 2.69 Å for the Me, Et, ^{i}Pr, and $SiMe_3$ structures, respectively, with La−C distances ranging from 2.857 (3) to 3.029 (2) Å. Despite the steric crowding, ligand exchange can be observed by NMR spectroscopy.

Introduction

Recent studies of the chemistry of tris(pentamethylcyclopentadienyl) complexes of samarium,[1−4] neodymium,[5,6] and uranium[7,8] have shown that the extreme steric crowding present in these molecules can lead to high reactivity of two general types. With certain substrates, the $(C_5Me_5)_3M$ complexes behave like bulky alkyl compounds in which one of the rings displays η^1 behavior, i.e., $(\eta^5\text{-}C_5Me_5)_2M(\eta^1\text{-}C_5Me_5)$, and insertion chemistry is observed. With other substrates, reduction chemistry is found, which can be explained by a $C_5Me_5^-/C_5Me_5$ redox couple as shown in eq 1.

$$(C_5Me_5)_3M \rightarrow e^- + [(C_5Me_5)_2M]^+ + 1/2(C_5Me_5)_2 \quad (1)$$

Since this type of reactivity apparently derives from the steric crowding, it has been called sterically induced reduction.[9]

Although the Sm(III), Nd(III), and U(III) ions in the $(C_5Me_5)_3M$ complexes synthesized thus far are paramagnetic, NMR spectroscopy has proven to be useful in characterizing the existence of new products and new patterns of tris(cyclopentadienyl) reactivity. However, definitive characterization of the reaction products by NMR spectroscopy was limited by the paramagnetism, and ultimate identification of the reaction products relied on X-ray crystallography. The paramagnetism also precluded some types of NMR-based reactivity studies. In efforts to obtain a diamagnetic system more amenable to NMR spectroscopic analysis, we have attempted to synthesize sterically crowded tris(peralkylcyclopentadienyl) complexes of La^{3+}.

Since lanthanum is the largest of the lanthanides,[10] it was expected that the complex $(C_5Me_5)_3La$ should be sterically accessible. However, since the high reactivity of the $(C_5Me_5)_3M$ complexes prepared to date is correlated with steric crowding, it was not clear that $(C_5Me_5)_3La$, with its larger metal, would be crowded enough to have the interesting chemistry of the other $(C_5Me_5)_3M$ complexes. Previously, it had been found that the

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ansa complex $Me_2Si(C_5Me_4)_2Sm(C_5Me_5)$,[11] which is less crowded than $(C_5Me_5)_3Sm$, has none of the alkyl or reduction reactivity of $(C_5Me_5)_3Sm$. In addition, the less-crowded $(C_5Me_5)_3Nd$ was found to be a weaker reductant than $(C_5Me_5)_3Sm$.[6]

For these reasons, we sought to synthesize a series of $(C_5Me_4R)_3La$ complexes in which R is an alkyl or silyl group that is larger than methyl. Given the difficulties in synthesizing and definitively characterizing the first four examples of tris(peralkylcyclopentadienyl)metal in the literature, namely, $(C_5Me_5)_3Nd$,[5] $(C_5Me_5)_3U$,[12] $(C_5Me_5)_3Sm$,[4] and $(C_5Me_4Et)_3Sm$,[13] it was not clear if such $(C_5Me_4R)_3La$ complexes could be obtained, much less crystallized for detailed structural analysis. We report here the successful synthesis and structural characterization of examples in which the R = Me, Et, ^iPr, and $SiMe_3$. To our knowledge, this is the first fully characterized lanthanide complex utilizing the $C_5Me_4SiMe_3^-$ ligand in the literature.[14]

Experimental Section

The complexes described below are extremely air and moisture sensitive. Therefore, the syntheses and manipulations of these compounds were conducted under nitrogen or argon with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. Since the $(C_5Me_4R)_3Ln$ complexes can react with THF, all manipulations involving these complexes were done under THF-free conditions. All reaction chemistry was done in glassware silylated using Siliclad (Gelest) diluted to 1% in deionized water. Solvent drying and physical measurements have been described previously.[15,16] Anhydrous lanthanum trichloride was used as received from Strem Chemicals. C_5Me_4EtH,[17] $C_5Me_4{}^iPrH$,[18] and $C_5Me_4SiMe_3H$[19] were prepared according to literature methods. KC_5Me_4R and LiC_5Me_4R (R = Et, ^iPr, $SiMe_3$) were prepared by reaction of the respective cyclopentadienes with KH in THF or 10% excess *n*-BuLi in hexanes. Allylmagnesium chloride (2.0 M in THF) was used as received from Aldrich. $(C_5Me_5)_2La(BPh_4)$ was prepared according to the literature method.[5] ^1H and ^{13}C NMR spectra were obtained on a Bruker DRX 400 or Omega 500 MHz spectrometer at 25 °C. Infrared analyses were acquired as thin films using an Applied Systems ReactIR 1000 instrument. Elemental analyses were performed by Analytische Laboratorien, Lindlar (Germany), or by complexometric titration.[20]

$(C_5Me_4Et)_2LaCl_2K(THF)_2$, 1. In a nitrogen glovebox, $LaCl_3$ (0.690 g, 2.81 mmol) and $K(C_5Me_4Et)$ (1.06 g, 5.63 mmol) were stirred in THF for 24 h. The resulting white slurry was filtered to yield a pale yellow solution. The solvent was removed under vacuum to yield **1** (1.02 g, 53%) as a white solid. ^1H NMR (C_6D_6): δ 3.57 (m, 6 H), 2.64 (q, 4 H), 2.22 (s, 12 H), 2.18 (s, 12 H), 1.39 (m, 6 H), 1.18 (t, 6 H). Anal. Calcd for $LaKCl_2O_2C_{30}H_{50}$: La, 20.0. Found: La, 19.6.

$(C_5Me_4{}^iPr)_2LaCl_2K(THF)_2$, 2. As described for **1**, $LaCl_3$ (0.439 g, 1.79 mmol) and $K(C_5Me_4{}^iPr)$ (0.724 g, 3.58 mmol) were reacted to yield **2** (1.13 g, 92%) as a white solid. ^1H NMR (C_6D_6): δ 3.56 (m, 4 H), 3.24 (m, 2 H), 2.30 (s, 14 H), 2.15 (s, 13 H), 1.40 (m, 14 H), 1.35 (m, 4 H). Anal. Calcd for $LaKCl_2O_2C_{32}H_{54}$: La, 19.3. Found: La, 19.5.

$(C_5Me_4SiMe_3)_2LaCl_2K(THF)_2$, 3. As described for **1**, $LaCl_3$ (0.794 g, 3.24 mmol) and $K(C_5Me_4SiMe_3)$ (1.50 g, 6.48 mmol) were reacted to yield **3** (1.55 g, 62%) as a white solid. ^1H NMR (C_6D_6): δ 3.55 (m, 9 H), 1.90 (s, 6 H), 1.80 (s, 6 H), 1.40 (m, 9 H), −0.03 (s, 9 H). Anal. Calcd for $LaSi_2KCl_2O_2C_{32}H_{58}$: La, 17.8. Found: La, 18.1.

$(C_5Me_4Et)_2La(CH_2CHCH_2)$, 4. In a nitrogen glovebox, $ClMg(CH_2CHCH_2)$ (1.35 mL of a 2.2 M solution in THF, 2.97 mmol) was added to a stirring slurry of $(C_5Me_4Et)_2LaCl_2K(THF)_2$ (1.71 g, 2.48 mmol) in toluene (~50 mL). The white slurry immediately became a yellow solution. After 1 h, the solvent was removed by rotary evaporation to yield a bright yellow solid. This material was triturated with 2% dioxanes in hexanes (75 mL) and filtered through a coarse frit to yield an orange solution. After removal of the solvent, the yellow solid was dried under high vacuum (1×10^{-5} Torr) for 24 h at 35−45 °C to remove coordinated THF. The resulting material was extracted with hexanes to yield **4** (1.12 g, 94%) upon solvent removal. ^1H NMR (C_6D_6): δ 6.48 (m, CH_2CHCH_2, 1 H), 3.10 (d, J_{HH} = 15 Hz, *anti*-CH_2CHCH_2, 2 H), 2.65 (d, J_{HH} = 9 Hz, *syn*-CH_2CHCH_2, 2 H), 2.36 (q, -CH_2CH_3, 4 H), 1.99 (s, 12 H), 1.90 (s, 12 H), 0.88 (t, -CH_2CH_3, 6 H).

$(C_5Me_4{}^iPr)_2La(CH_2CHCH_2)$, 5. As described for **4**, $(C_5Me_4{}^iPr)_2LaCl_2Li(THF)_2$ (1.94 g, 2.83 mmol) was reacted with $ClMg(CH_2CHCH_2)$ (1.6 mL of a 2.2 M solution in THF, 2.6 mmol) to yield **5** as a yellow solid (0.910 g, 64%). ^1H NMR (C_6D_6): δ 6.29 (m, CH_2CHCH_2, 1 H), 2.88 (d, J_{HH} = 15 Hz, *anti*-CH_2CHCH_2, 2 H), 2.75 (m, -$CH(CH_3)_2$, 1 H), 2.69 (m, -$CH(CH_3)_2$, 1 H), 2.59 (d, J_{HH} = 9 Hz, *syn*-CH_2CHCH_2, 2 H), 2.02 (s, 6 H), 1.99 (s, 6 H), 1.77 (s, 6 H), 1.72 (s, 6 H), 0.88 (d, J_{HH} = 7 Hz, 6 H), 0.83 (d, J_{HH} = 7 Hz, 6 H). IR: 2957 s, 2922 s, 2864 s, 2725 m, 1544 s, 1444 s, 1382 s, 1258 s, 1239 s, 1100 s, 1019 s, 876 m, 802 s, 776 s cm^{-1}.

$(C_5Me_4SiMe_3)_2La(CH_2CHCH_2)$, 6. As described for **4**, $(C_5Me_4SiMe_3)_2LaCl_2K(THF)_2$ (1.554 g, 2.00 mmol) was reacted with $ClMg(CH_2CHCH_2)$ (1.5 mL of a 2.2 M solution in THF, 3.0 mmol) to yield **6** (1.12 g, 94%) upon solvent removal. ^1H NMR (C_6D_6): δ 6.48 (m, CH_2CHCH_2, 1 H), 3.16 (d, J_{HH} = 12 Hz, *anti*-CH_2CHCH_2, 2 H), 2.76 (d, J_{HH} = 8 Hz, *syn*-CH_2CHCH_2, 2 H), 2.26 (s, 6 H), 2.20 (s, 6 H), 1.89 (s, 6 H), 1.85 (s, 6 H), 0.21 (s, 9 H), 0.18 (s, 9 H). ^{13}C NMR (C_6D_6): δ 151.4, 127.7, 124.3, 124.2, 116.3, 116.0, 76.3, 14.8, 14.6, 11.4, 11.2, 1.6, 1.2. IR: 2953 s, 2922 s, 2856 s, 1544 m, 1477 s, 1324 s, 1247 s, 1092 s, 1019 s, 838 m, 803 m, 753 m, 683 m cm^{-1}.

$[(C_5Me_4Et)_2La][BPh_4]$, 7. In an argon-filled glovebox, **4** (0.145 g, 0.303 mmol) and Et_3NHBPh_4 (0.193 g, 0.454 mmol) were stirred in benzene (~10 mL) for 12 h. Excess Et_3NHBPh_4 was removed by centrifugation, yielding a pale yellow solution. Complex **7** was isolated as a pale yellow solid after removal of the solvent (0.212 g, 92%). ^1H NMR (C_6D_6): δ 7.71 (d, J_{HH} = 6.8 Hz, *m*-C_6H_5, 8 H), 7.21 (t, J_{HH} = 7.2 Hz, *o*-C_6H_5, 8 H), 7.08 (t, J_{HH} = 7.2 Hz, *p*-C_6H_5, 4 H), 2.13 (q, 4 H), 1.66 (s, 12 H), 1.58 (s, 12 H), 0.74 (t, 6 H).

$[(C_5Me_4{}^iPr)_2La][BPh_4]$, 8. As described for **7**, $(C_5Me_4{}^iPr)_2La(CH_2CHCH_2)$ (0.910 g, 1.80 mmol) was reacted with excess Et_3NHBPh_4 (0.989 g, 2.337 mmol) to yield **8** as a pale yellow solid (1.409 g, 99%). ^1H NMR (C_6D_6): δ 7.73 (d, J_{HH} = 6 Hz, *m*-C_6H_5, 8 H), 7.24 (t, J_{HH} = 7.6 Hz, *o*-C_6H_5, 8 H), 7.13 (t, J_{HH} = 7.2 Hz, *p*-C_6H_5, 4 H), 2.7.6 (m, 2 H), 1.87 (s, 12 H), 1.51 (s, 12 H), 1.01 (d, J_{HH} = 7.2 Hz, 12 H).

$[(C_5Me_4SiMe_3)_2La][BPh_4]$, 9. As described for **7**, $(C_5Me_4SiMe_3)_2La(CH_2CHCH_2)$ (0.097 g, 0.17 mmol) was reacted with Et_3NHBPh_4 (0.094 g, 0.22 mmol) to yield **9** (0.145 g, 95%) as a pale yellow solid. ^1H NMR (C_6D_6): δ 7.71 (d, J_{HH} = 6.0 Hz, *m*-C_6H_5, 8 H), 7.28 (t, J_{HH} = 7.0 Hz, *o*-C_6H_5, 8 H), 7.13 (t, J_{HH} = 7.0 Hz, *p*-C_6H_5, 4 H), 1.97 (s, 12 H), 1.46 (s, 12 H), 0.23 (s, 18 H). ^{13}C NMR (C_6D_6): δ 136.1, 134.3, 130.2, 129.4, 126.8, 126.2, 123.44, 15.0, 11.7, 2.7.

$(C_5Me_5)_3La$, 10. In an argon-filled glovebox, $(C_5Me_5)_2La(BPh_4)$ (0.938 g, 1.29 mmol) was stirred with KC_5Me_5 (0.246 g, 1.42 mmol) in benzene (~10 mL) for 24 h. Insoluble materials were removed by centrifugation, and the solvent was removed from the resulting yellow solution by rotary evaporation to yield **10** (0.552 g, 79%) as a bright yellow solid. ^1H NMR (C_6D_6): δ 1.997. ^{13}C NMR (C_6D_6): δ 122.0, 12.5. IR: 2961 s, 2907 s, 2856 s, 1478 s, 1440 s, 1378 s, 1251 s, 1154 s, 1034 s, 946 m, 926 m, 714 s, 675 m cm^{-1}. Anal. Calcd for $LaC_{30}H_{45}$: La, 25.51; C, 66.17; H, 8.32. Found: La, 27.25; C, 64.09;

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Table 1. X-ray Data Collection Parameters for (C$_5$Me$_5$)$_3$La, **10**, (C$_5$Me$_4$Et)$_3$La, **11**, (C$_5$Me$_4$^{i}Pr)$_3$La, **12**, and (C$_5$Me$_4$SiMe$_3$)$_3$La, **13**

	10	**11**	**12**	**13**
formula	C$_{30}$H$_{45}$La	C$_{33}$H$_{51}$La	C$_{36}$H$_{57}$La	C$_{36}$H$_{63}$Si$_3$La•C$_7$H$_8$
fw	544.57	586.65	628.73	811.18
space group	$P6_3/m$	$P\bar{1}$	$C2/c$	$P\bar{1}$
crystal system	hexagonal	triclinic	monoclinic	triclinic
a (Å)	10.1019 (4)	10.0459 (5)	35.675 (3)	10.2192 (7)
b (Å)		10.0786 (5)	10.2853 (8)	10.2734 (7)
c (Å)	15.5214 (8)	16.1832 (8)	18.7528 (14)	20.4975 (14)
α (deg)		90.3550 (10)		96.1360 (10)
β (deg)		90.1080 (10)	112.2890 (10)	98.3940 (10)
γ (deg)		118.8050 (10)		91.8110 (10)
V (Å^3)	1371.73 (10)	1435.73 (12)	6366.9 (8)	2114.3 (3)
Z	2	2	8	2
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (Mg/m^3)	1.318	1.357	1.312	1.274
μ (Mo Kα) (mm^{-1})	1.571	1.506	1.363	1.123
temp (K)	183	158	163	158
R^a ($I > 2\sigma(I)$): R1	0.0206	0.0297	0.0355	0.0240
R^b (all data): wR2	0.0609	0.0722	0.0980	0.0637

^{a} $\mathrm{R1} = \sum||F_0| - |F_c||/\sum|F_0|$. ^{b} $\mathrm{wR2} = [\sum[w(F_0{}^2 - F_c{}^2)^2]/\sum(w(F_0{}^2)^2)]^{1/2}$.

H, 8.12. Single crystals suitable for X-ray diffraction were obtained by cooling a hot toluene solution to room temperature.

(C$_5$Me$_4$Et)$_3$La, 11. As described for **10**, [(C$_5$Me$_4$Et)$_2$La][BPh$_4$] (0.196 g, 0.26 mmol) was stirred with KC$_5$Me$_4$Et (0.083 g, 0.440 mmol) to form **11** (0.129 g, 85%). ^{1}H NMR (C$_6$D$_6$): δ 2.53 (q, -C*H*$_2$CH$_3$, 6 H), 2.15 (s, 14 H), 2.03 (s, 14 H), 1.10 (t, 2 H), 0.91 (t, 7 H). ^{13}C NMR (C$_6$D$_6$): δ 126.3, 124.2, 122.0, 121.0, 118.5, 117.5, 19.7, 19.5, 15.4, 14.1, 13.8, 12.4, 11.4, 11.3. IR: 2960 s, 2910 s, 2856 s, 2721 m, 1449 s, 1378 s, 1368 s, 1310 s, 1258 s, 1050 s, 1019 s, 972.5 m, 800 m cm^{-1}. Anal. Calcd for LaC$_{33}$H$_{51}$: La, 23.67; C, 67.55; H, 8.76. Found: La, 22.55; C, 67.85; H, 8.29. Single crystals suitable for X-ray diffraction were obtained by cooling a hot toluene solution to room temperature.

(C$_5$Me$_4$^{i}Pr)$_3$La, 12. As described for **10**, [(C$_5$Me$_4$^{i}Pr)$_2$La][BPh$_4$] (0.724 g, 0.93 mmol) was reacted with KC$_5$Me$_4$^{i}Pr (0.225 g, 1.11 mmol) to yield **12** as a yellow solid (0.499 g, 85%). ^{1}H NMR (C$_6$D$_6$): δ 3.11 (s, $J_{\mathrm{HH}} = 7.2$ Hz, -C*H*-(CH$_3$)$_2$, 3 H), 2.29 (s, 17.6 H), 2.27 (s, 0.7 H), 2.07 (s, 0.6 H), 2.02 (s, 17.6 H), 1.26 (d, 0.8 H), 1.15 (d, 17.8 H). ^{13}C NMR (C$_6$D$_6$): δ 129.2, 123.8, 121.2, 27.0, 22.0, 14.4, 12.0. IR: 2961 s, 2914 s, 2868 s, 1444 s, 1363 s, 1382 s, 1380 s, 1262 s, 1100 s, 1031 s, 803 s, 745 s, 714 s, 676 s cm^{-1}. Anal. Calcd for LaC$_{36}$H$_{57}$: La, 22.09; C, 68.78; H, 9.13. Found: La, 22.05; C, 69.02; H, 8.54. Single crystals suitable for X-ray diffraction were obtained by cooling a hot toluene solution to room temperature.

(C$_5$Me$_4$SiMe$_3$)$_3$La, 13. As described for **10**, [(C$_5$Me$_4$SiMe$_3$)$_2$La][BPh$_4$] (0.948 g, 1.12 mmol) reacted with KC$_5$Me$_4$SiMe$_3$ (0.260 g, 1.12 mmol) to yield **13** as a light yellow solid (0.473 g, 59%). ^{1}H NMR (C$_6$D$_6$): δ 2.36 (s, 18 H), 2.01 (s, 18 H), 0.36 (s, 27 H). ^{13}C NMR (C$_6$D$_6$): δ 134.0, 126.2, 118.4, 17.4, 13.0, 3.1. IR: 2953 s, 2914 s, 2860 s, 1444 s, 1324 s, 1247 m, 1127 s, 1019 m, 984 s, 837 s, 753 m, 676 m cm^{-1}. Anal. Calcd for LaSi$_3$C$_{36}$H$_{63}$: La, 19.32; Si, 11.72; C, 60.14; H, 8.23. Found: La, 19.50; Si, 10.15; C, 61.60; H, 8.63. Single crystals suitable for X-ray diffraction were obtained by cooling a hot toluene solution to room temperature.

Exchange Reaction of 10 and 13. Complexes **10** (0.0065 g, 0.013 mmol) and **13** (0.0096 g, 0.012 mmol) were dissolved in C$_6$D$_6$. ^{1}H NMR spectroscopy indicated no reaction after mixing. After 12 h, two new sets of peaks were observed, set **A** at δ 2.327, 2.050, 1.984, and 0.329 ppm and set **B** at 2.314, 2.020, 1.934, and 0.307 ppm, along with the starting materials. Six days of reaction left 5% of **10** and 10% of **13**. ^{1}H NMR spectroscopy indicated a 1.6:1 ratio of **A**:**B**. See Figure 6 in Supporting Information for a series of representative spectra displaying this exchange.

X-ray Data Collection, Structure Determination, and Refinement for the (C$_5$Me$_4$R)$_3$La Complexes 10−13. In all cases, a yellow crystal, of dimensions reported in Table 1, was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[21] program package was used to determine the unit-cell parameters and for data collection. A 20 s/frame scan time for a sphere of diffraction data was collected on complexes **10** and **11**; a 30 s/frame scan time for a hemisphere of data was collected on complex **12**, and a 30 s/frame scan time for a sphere of data was collected on complex **13**. The raw frame data were processed using SAINT[22] and SADABS[23] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[23] program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[24] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference Fourier map and refined (x,y,z and U_{iso}) or were included using a riding model.

(C$_5$Me$_5$)$_3$La, 10. The systematic absences were consistent with the hexagonal space groups $P6_3$ and $P6_3/m$. It was later determined that the centrosymmetric space group $P6_3/m$ was correct. The molecule was located on a site of $\bar{6}$ symmetry. At convergence, wR2 = 0.0609 and GOF = 1.201 for 52 variables refined against 1164 unique data. As a comparison for refinement on F, R1 = 0.0206 for those 1133 data with $I > 2.0\sigma(I)$.

(C$_5$Me$_4$Et)$_3$La, 11. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. At convergence, wR2 = 0.0722 and GOF = 1.233 for 511 variables refined against 6754 unique data. As a comparison for refinement on F, R1 = 0.0297 for those 6383 data with $I > 2.0\sigma(I)$.

(C$_5$Me$_4$^{i}Pr)$_3$La, 12. The diffraction symmetry was $2/m$, and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that the centrosymmetric space group $C2/c$ was correct. At convergence, wR2 = 0.0980 and GOF = 1.111 for 562 variables refined against 7596 unique data. As a comparison for refinement on F, R1 = 0.0355 for those 6698 data with $I > 2.0\sigma(I)$.

(C$_5$Me$_4$SiMe$_3$)$_3$La, 13. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. There was one molecule of toluene solvent present per formula unit. At convergence, wR2 = 0.0637 and GOF = 1.100 for 676 variables refined against 9905 data. As a comparison for refinement on F, R1 = 0.0226 for those 9502 data with $I > 2.0\sigma(I)$.

Results

Synthetic Background. Although it was originally thought that (C$_5$Me$_5$)$_3$Sm complexes were too sterically crowded to exist,

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(21) *SMART Software User's Guide*, version 4.21; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

(22) *SAINT Software User's Guide*, version 4.05; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

(23) Sheldrick, G. M. *SHELXTL*, version 5.10; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

(24) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992.

there now exist four separate syntheses (eqs 2−5).[4,5,12,13] Since two of these syntheses rely on the special reduction chemistry of Sm(II) (eqs 2 and 3), only two precedented routes were available for a trivalent lanthanide such as La(III).

$$2(C_5Me_5)_2Sm + C_8H_8 \rightarrow (C_5Me_5)_3Sm + (C_5Me_5)Sm(C_8H_8) \quad (2)$$

$$2(C_5Me_5)_2Sm(OEt_2) + (C_5Me_5)_2Pb \rightarrow 2(C_5Me_5)_3Sm + Pb + 2OEt_2 \quad (3)$$

$$[(C_5Me_5)_2SmH]_2 + 2C_{10}H_{14} \rightarrow 2(C_5Me_5)_3Sm \quad (4)$$

$$[(C_5Me_5)_2Sm][BPh_4] + K(C_5Me_5) \rightarrow (C_5Me_5)_3Sm + KBPh_4 \quad (5)$$

Given the limited stability of the $[(C_5Me_5)_2LnH]_2$ lanthanide hydrides,[25−28] the best of the trivalent syntheses of $(C_5Me_5)_3Ln$ complexes appears to be the reaction of the unsolvated cation, $[(C_5Me_5)_2Ln][BPh_4]$, with $K(C_5Me_5)$ shown in eq 5.

To make $(C_5Me_4R)_3La$ complexes starting from $LaCl_3$ by this route,[5] four separate reactions are required, as shown in eqs 6−9.

$$2K(C_5Me_4R) + LaCl_3 \rightarrow (C_5Me_4R)_2LaCl_2K(THF)_2 + KCl \quad (6)$$

$$(C_5Me_4R)_2LaCl_2K(THF)_2 + (allyl)MgCl \rightarrow (C_5Me_4R)_2La(CH_2CHCH_2) + MgCl_2 + KCl \quad (7)$$

$$(C_5Me_4R)_2La(CH_2CHCH_2) + Et_3NHBPh_4 \rightarrow [(C_5Me_4R)_2La][BPh_4] + Et_3N + CH_3CH{=}CH_2 \quad (8)$$

$$[(C_5Me_4R)_2La][BPh_4] + KC_5Me_4R \rightarrow (C_5Me_4R)_3La + KBPh_4 \quad (9)$$

Although both $(C_5Me_5)_3Sm$ and $(C_5Me_5)_3Nd$ were made by this route, initial attempts to make the lanthanum analogue, the least sterically crowded member of the $(C_5Me_5)_3Ln$ series, failed. It was not until these reactions were conducted in silylated glassware, as described below, that the synthesis was a success.

$(C_5Me_4R)_3La$ Syntheses. In the first step of the synthesis, eq 6, formation of the $(C_5Me_4R)_2LaCl_2K(THF)_2$ “ate” salts from $LaCl_3$ and KC_5Me_4R was accomplished following the traditional procedure for introducing a C_5R_5 ligand into a lanthanide ion coordination sphere.[27,29,30] The synthesis of the $(C_5Me_4R)_2LaCl_2K(THF)_2$ complexes was nearly identical to the route used for formation of $(C_5Me_5)_2LaCl_2Li(Et_2O)_2$,[27] except that heating the reaction mixture at reflux was found to be unnecessary. The use of the KC_5Me_4R salts rather than LiC_5Me_4R gave slightly better yields (53−62%) than those previously reported for $(C_5Me_5)_2LaCl_2Li(Et_2O)_2$ (49%). The ^1H NMR spectra of complexes **1**−**3** contained the pattern expected for the C_5Me_4R ligand and coordinated THF.

The second step of the synthesis involved conversion of salts **1**−**3** to complexes that could be readily transformed into solvent-free cations via protonolysis with $[Et_3NH][BPh_4]$ or a similar reagent. Prior work on the synthesis of $(C_5Me_5)_3Nd$ showed that the allyl complex $(C_5Me_5)_2Nd(CH_2CHCH_2)$ was a better synthetic precursor to form the cationic complex, $[(C_5Me_5)_2Nd][BPh_4]$, than the commonly used hydrocarbyl species $(C_5Me_5)_2Nd[CH(SiMe_3)_2]$.[5] Solvent-free $(C_5Me_4R)_2La(CH_2CHCH_2)$ complexes were made from the $(C_5Me_4R)_2LaCl_2K(THF)_2$ complexes using allylmagnesium chloride as shown in eq 7.

Like their C_5Me_5 analogue $(C_5Me_5)_2La(CH_2CHCH_2)$, complexes **4**−**6** are very soluble in alkanes, arenes, and coordinating solvents. However, the $(C_5Me_4Et)_2La(CH_2CHCH_2)$ and $(C_5Me_4{}^iPr)_2La(CH_2CHCH_2)$ complexes lost THF with greater facility, requiring only mild temperatures (35−45 °C) and desolvation times (24 h). In comparison, $(C_5Me_5)_2La(CH_2CHCH_2)$ required temperatures of 55−65 °C and 48 h. In the R = $SiMe_3$ case, isolation of a solvent-free allyl complex was facile: complex **6**, $(C_5Me_4SiMe_3)_2La(CH_2CHCH_2)$, did not readily coordinate THF and was easily crystallized from hexanes as a solvent-free complex. Evidently, the increased steric bulk around the metal center in **6** prevents effective coordination of the solvent.

The third step of the synthesis involved protonation of the allyl units in $(C_5Me_4R)_2La(CH_2CHCH_2)$ to form the cations $[(C_5Me_4R)_2La][BPh_4]$ (eq 8). This was readily accomplished in benzene at room temperature yielding complexes **7**−**9**. The ^1H NMR spectra for these complexes contained one set of resonances for the tetraphenylborate protons and one set of peaks for the equivalent C_5Me_4R ligands. The identities of complexes **7** and **9** were confirmed by X-ray crystallographic analysis[31] and found to be similar to the structure of $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$.[5]

The final step in the syntheses was the reaction of KC_5Me_4R with the cationic complexes **7**−**9** (eq 9). The $(C_5Me_4R)_3La$ (R = Et, ^iPr, $SiMe_3$) complexes, **11**−**13**, were formed by this route in benzene after the solutions were stirred for 24 h at room temperature. Each was isolated as a bright yellow powder and characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy and X-ray crystallography.

Special Aspects of $(C_5Me_5)_3La$. In contrast, the synthesis of the R = Me complex $(C_5Me_5)_3La$ was more difficult. Although a bright yellow product, **10**, similar to **11**−**13**, could be isolated and displayed a single ^1H NMR resonance as expected for $(C_5Me_5)_3La$ (1.997 ppm), initial attempts to confirm the existence of $(C_5Me_5)_3La$ by X-ray crystallography failed. Crystallization attempts with this yellow product provided, instead, the bridged oxide, $[(C_5Me_5)_2La]_2(\mu\text{-}O)$, which could be fully characterized by X-ray diffraction studies.[31] The structure of this oxide is similar to that of $[(C_5Me_5)_2Sm]_2O$,[32] which is also a common byproduct of reactions involving $(C_5Me_5)_2Sm$ units.

This $(C_5Me_5)_3La$ system was complicated by the fact that the oxide had a single ^1H NMR resonance at 2.02 ppm, which was very close to that of $(C_5Me_5)_3La$ at 1.997 ppm. Even in a sealed NMR tube, the 1.997 ppm product was observed to convert to the 2.02 ppm oxide contaminant. For example, 16% conversion was observed after 3 days at room temperature. However, when the $[(C_5Me_5)_2La][BPh_4]/KC_5Me_5$ reaction was run in silylated glassware and the product was handled in silylated glassware, the formation of the oxide decomposition product was minimized. Following this discovery, reactions 6−9 were conducted in silylated glassware, and this resulted in the full characterization of $(C_5Me_5)_3La$. It is interesting to note that the *least* sterically crowded of the $(C_5Me_5)_3Ln$ complexes

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(25) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401−1403.
(26) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51−66.
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(32) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405−409.

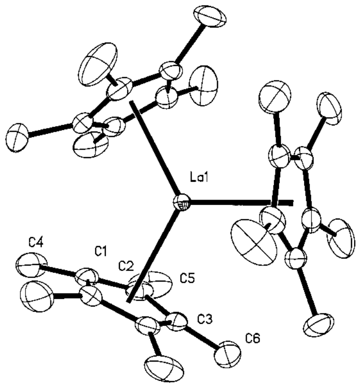

Figure 1. Thermal ellipsoid plot of $(C_5Me_5)_3La$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

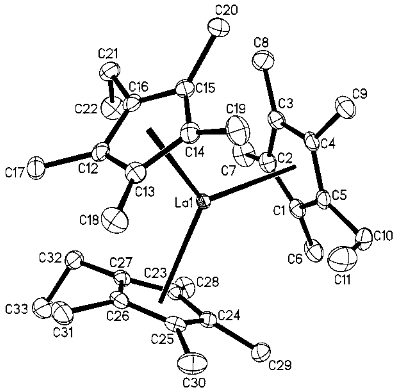

Figure 2. Thermal ellipsoid plot of $(C_5Me_4Et)_3La$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

(Ln = La, Nd, Sm)[4,5] was the most difficult to isolate in a pure crystalline form. Silylated glassware was not necessary in the synthesis of the $(C_5Me_5)_3Nd$ and $(C_5Me_5)_3Sm$ analogues.

Structural Data. Although the spectroscopic data supported the formation of the $(\eta^5\text{-}C_5Me_4R)_3La$ products, the rather simple ^1H NMR spectra of the complexes were not definitive. Only the simple resonance patterns of the C_5Me_4R moieties were observed. This made it difficult to distinguish the desired $(\eta^5\text{-}C_5Me_4R)_3La$ complexes and the bimetallic oxide-bridged decomposition products $[(\eta^5\text{-}C_5Me_4R)_2La]_2O$. For this reason, we undertook X-ray diffraction studies to confirm the existence of these molecules. In addition, it seemed prudent to obtain the crystallographic data, given that for decades it was assumed that it was not possible to put three C_5Me_5 rings around any metal. The structural data were also needed to provide critical information on the orientation of the R substituent and the relative amount of steric congestion as the R group increases in size.

Fortunately, good single crystals could be obtained for $(C_5Me_5)_3La$ (**10**), $(C_5Me_4Et)_3La$ (**11**), $(C_5Me_4{}^iPr)_3La$ (**12**), and $(C_5Me_4SiMe_3)_3La$ (**13**), as shown in Figures 1−4, respectively. Crystallographic cell parameters are provided in Table 1, and a comprehensive summary of structural features of the $(C_5Me_4R)_3La$ complexes is given in Table 2. Comparisons with related complexes are given in Tables 3 and 4. $(C_5Me_5)_3La$, **10**, Figure 1, is isomorphous with $(C_5Me_5)_3Nd$,[5] $(C_5Me_5)_3Sm$,[4] and $(C_5Me_5)_3U$.[12] $(C_5Me_4Et)_3La$, **11**, Figure 2, is isomorphous with $(C_5Me_4Et)_3Sm$.[13]

The structure of $(C_5Me_5)_3La$ will be discussed first, since it provides a basis for comparing the effect of introducing the substituent R in the other C_5Me_4R structures. Table 3 compares $(C_5Me_5)_3La$ with the two other $(C_5Me_5)_3Ln$ structures in the literature and shows that $(C_5Me_5)_3La$ has the metrical parameters expected on the basis of the larger size of La^{3+}. Subtraction of each average Ln−C(ring) distance from the nine coordinate metal ion radius gives a nearly constant difference in the 1.697−1.688 Å range as is typical of isomorphous organo-f-element complexes.[33]

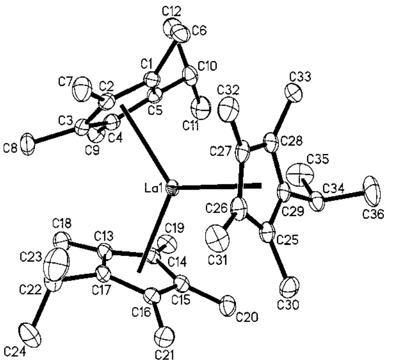

Figure 3. Thermal ellipsoid plot of $(C_5Me_4{}^iPr)_3La$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

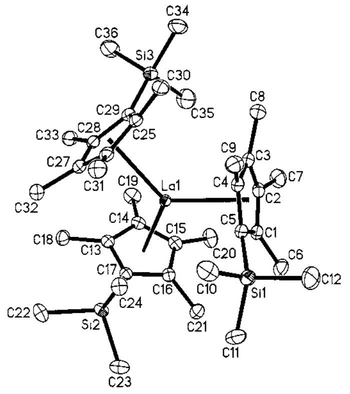

Figure 4. Thermal ellipsoid plot of $(C_5Me_4SiMe_3)_3La$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and toluene are omitted for clarity.

In all of these $(C_5Me_5)_3Ln$ structures, the three rings are crystallographically equivalent and the three ring centroids define a trigonal planar geometry around the metal with 120° (ring centroid)−M−(ring centroid) angles. Within each ring, there are just three crystallographically unique ring carbon positions. In $(C_5Me_5)_3La$, these carbon atoms have La−C distances of 2.975 (3), 2.896 (2), and 2.873 (2) Å for C(1), C(2), and C(3), respectively. Each of the methyl carbons attached to these ring carbons lies out of the plane of the ring carbons. The displacements are 0.501, 0.160, and 0.309 Å for the methyl carbon atoms attached to C(1), C(2), and C(3), respectively. Hence, the size of the displacement does not correlate with the length of the La−C bond. These displacements can be compared to the analogous displacements of 0.521, 0.175, and 0.362 Å in $(C_5Me_5)_3Sm$. Hence, the larger La system leads to smaller out of plane displacements than for Sm. Displacements of 0.09−0.31 Å have been observed in other types of less-crowded $(C_5Me_5)_3Ln$ complexes.[34−36]

Table 4 compares the $(C_5Me_4R)_3La$ structures with those of $(C_5Me_5)_3La$ and $(C_5Me_4Et)_3Sm$. Complexes **11** (R = Et) and

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Table 2. Selected Bond Distances (Å) and Angles (deg) for (C$_5$Me$_5$)$_3$La, **10**, (C$_5$Me$_4$Et)$_3$La, **11**, (C$_5$Me$_4$^{i}Pr)$_3$La, **12**, and (C$_5$Me$_4$SiMe$_3$)$_3$La, **13**

10		**11**		**12**		**13**	
La–C(1)	2.975 (3)	La–C(1)	2.973 (3)	La–C(1)	2.928 (3)	La–C(1)	3.029 (2)
La–C(2)	2.896 (2)	La–C(2)	2.932 (3)	La–C(2)	2.893 (3)	La–C(2)	2.962 (2)
La–C(3)	2.873 (2)	La–C(3)	2.913 (3)	La–C(3)	2.921 (3)	La–C(3)	2.941 (2)
La–Cnt	2.642	La–C(4)	2.879 (3)	La–C(4)	2.933 (3)	La–C(4)	2.940 (2)
Cnt–La–Cnt	120.0	La–C(5)	2.878 (3)	La–C(5)	2.894 (3)	La–C(5)	2.957 (2)
		La–C(12)	2.876 (3)	La–C(13)	2.971 (3)	La–C(13)	3.018 (2)
		La–C(13)	2.921 (3)	La–C(14)	2.874 (3)	La–C(14)	2.986 (2)
		La–C(14)	2.948 (3)	La–C(15)	2.877 (3)	La–C(15)	2.923 (2)
		La–C(15)	2.960 (3)	La–C(16)	2.921 (3)	La–C(16)	2.890 (2)
		La–C(16)	2.857 (3)	La–C(17)	2.928 (3)	La–C(17)	2.906 (2)
		La–C(23)	2.869 (3)	La–C(25)	2.968 (3)	La–C(25)	2.988 (2)
		La–C(24)	2.899 (3)	La–C(26)	2.886 (3)	La–C(26)	2.952 (2)
		La–C(25)	2.907 (3)	La–C(27)	2.908 (3)	La–C(27)	2.948 (2)
		La–C(26)	2.966 (3)	La–C(28)	2.960 (3)	La–C(28)	2.925 (2)
		La–C(27)	2.909 (3)	La–C(29)	2.953 (3)	La–C(29)	2.925 (2)
		La–Cnt(1)	2.654	La(1)–Cnt(1)	2.652	La–Cnt(1)	2.706
		La–Cnt(2)	2.652	La–Cnt(2)	2.653	La–Cnt(2)	2.685
		La–Cnt(3)	2.654	La–Cnt(3)	2.674	La–Cnt(3)	2.687
		La···(11)	3.56	La···C(23)	4.01	La···C(24)	3.42
		La···C(22)	3.64	La···C(35)	4.10	La···C(35)	4.10
		Cnt(1)–La–Cnt(2)	119.8	Cnt(1)–La–Cnt(2)	119.5	Cnt(1)–La–Cnt(2)	120.3
		Cnt(1)–La–Cnt(3)	120.0	Cnt(1)–La–Cnt(3)	120.5	Cnt(1)–La–Cnt(3)	119.5
		Cnt(2)–La–Cnt(3)	120.2	Cnt(2)–La–Cnt(3)	120.0	Cnt(2)–La–Cnt(3)	119.7

Table 3. Comparison of Metrical Data for (C$_5$Me$_5$)$_3$Ln Complexes (M = La, Nd, and Sm)

	distance (Å)					
		metal-C (ring)				
(C$_5$Me$_5$)$_3$Ln	metal–centroid	high	low	mean	effective ionic radii (9 coordinate)[24]	[mean metal–C(ring)] – [ionic radius]
(C$_5$Me$_5$)$_3$La	2.642	2.975 (3)	2.8732 (19)	2.91 (5)	1.216	1.694
(C$_5$Me$_5$)$_3$Nd[5]	2.582	2.927 (2)	2.8146 (13)	2.86 (6)	1.163	1.697
(C$_5$Me$_5$)$_3$Sm[4]	2.555	2.910 (3)	2.782 (2)	2.82 (5)	1.132	1.688

Table 4. Comparison of Metrical Data for (C$_5$Me$_4$R)$_3$Ln Complexes (M = La and Sm)

	distance (Å)					
		metal-C (ring)				
(C$_5$Me$_4$R)$_3$Ln	metal–centroid mean	high	low	mean	effective ionic radius (9 coordinate)	[mean metal–C (ring)] – [ionic radius]
(C$_5$Me$_5$)$_3$La	2.642	2.975 (3)	2.8732 (2)	2.91 (5)	1.216	1.694
(C$_5$Me$_4$Et)$_3$La	2.653	2.973 (3)	2.857 (3)	2.91 (3)	1.216	1.694
(C$_5$Me$_4$^{i}Pr)$_3$La	2.659	2.971 (3)	2.874 (3)	2.92 (3)	1.216	1.704
(C$_5$Me$_4$SiMe$_3$)$_3$La	2.693	3.029 (2)	2.890 (2)	2.95 (3)	1.216	1.734
(C$_5$Me$_4$Et)$_3$Sm[13]	2.568	2.900 (14)	2.787 (12)	2.83 (4)	1.132	1.698

Table 5. Deviations from the C$_6$Me$_5$R Plane of the α-C (or Si) for Each Alkyl or Silyl Substituent (Atom Number Is in Brackets)

(C$_5$Me$_5$)$_3$La, **10**	(C$_5$Me$_4$Et)$_3$La, **11**	(C$_5$Me$_4$^{i}Pr)$_3$La, **12**	(C$_5$Me$_4$SiMe$_3$)$_3$La, **13**
0.501 [4]	0.481 [6]	0.479 [6]	0.542 [6]
0.160 [5]	0.196 [7]	0.185 [7]	0.236 [7]
0.309 [6]	0.314 [8]	0.314 [8]	0.313 [8]
	0.309 [9]	0.321 [9]	0.364 [9]
	0.053 [10]	0.174 [10]	0.498 [Si$_1$]
	0.340 [17]	0.491 [18]	0.458 [18]
	0.291 [18]	0.154 [19]	0.271 [19]
	0.246 [19]	0.338 [20]	0.279 [20]
	0.478 [20]	0.320 [21]	0.369 [21]
	0.030 [21]	0.113 [22]	0.161 [Si$_2$]
	0.277 [28]	0.496 [30]	0.447 [30]
	0.325 [29]	0.190 [31]	0.190 [31]
	0.207 [30]	0.312 [32]	0.342 [32]
	0.463 [31]	0.346 [33]	0.308 [33]
	0.249 [32]	0.154 [34]	0.190 [Si$_3$]

12 (R = ^{i}Pr) have a trigonal planar arrangement of C$_5$Me$_4$R rings around the metal with the ring centroids coplanar with La to within 0.001 Å. Complex **13** (R = SiMe$_3$) is distorted slightly toward a pyramidal geometry with the La 0.111 Å out of the plane. The structures of the Et and ^{i}Pr derivatives have bond distances similar to that of (C$_5$Me$_5$)$_3$La: neither the metal centroid distances nor the bond distances are very different. Only with the SiMe$_3$ derivative, **13**, do the absolute numbers increase, but they are still equivalent within the error limits. The differences between the average Ln–C(ring) distance and the metal radius for **11** and **12**, 1.694 and 1.704 Å, respectively, are similar to the 1.679–1.688 Å values for the (C$_5$Me$_5$)$_3$Ln complexes. Only for **13** does this value increase to 1.734 Å.

Examination of the displacements of the atoms attached to the ring carbons (Table 5) shows that each ring in compounds **10**–**13** has one large displacement value around 0.5 Å. As described above, (C$_5$Me$_5$)$_3$La has two other values of 0.309 and 0.160 Å. Complexes **11**–**13** appear to follow a somewhat similar pattern, i.e., they have two pairs in roughly this range, except for the atoms of the R group.

In (C$_5$Me$_4$Et)$_3$La, two of the ethyl carbon atoms attached directly to the ring have very small displacements (C(10), 0.0529 Å; C(21), 0.0296 Å). Both of these ethyl groups are also oriented so that their methyl groups point *toward* the La along the

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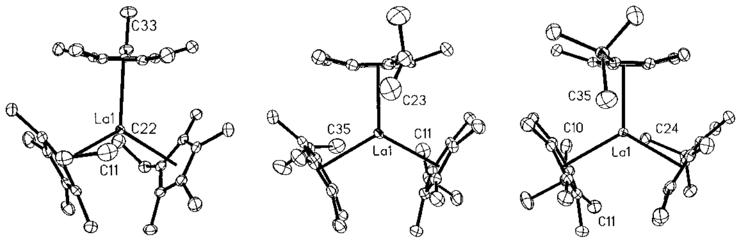

Figure 5. Complexes **11**−**13** viewed down the pseudo-C_3 axis.

pseudo-C_3 axis perpendicular to the plane of the metal and three ring centroids, as was found in $(C_5Me_4Et)_3Sm$ and as shown in Figure 5.

This puts the C(22) and C(11) atoms of the ethyl groups within 3.56 and 3.64 Å, respectively, of the metal center. In contrast, the other ethyl group points away from the metal. The carbon attached to that ring has a more “normal” displacement of 0.2485 Å, and C(33), the methyl carbon of the ethyl group, is 5.34 Å away from La.

To check if the different orientations of the ethyl groups arose due to some secondary packing, e.g., the effect of the CO-packing effect of the ligand substituents in metal carbonyl clusters on bridging vs terminal locations in the “ligand polyhedral model”,[37−39] the triangle defined by the three carbons C(10), C(21), and C(32) was examined. The triangle is not equilateral, and the lanthanum does not lie in the plane of this triangle. It is displaced by 0.506 Å. Hence, the orientation of the two ethyl groups toward the metal is not due to some “most efficient packing arrangement” of the ethyl part of the C_5Me_4-Et rings around the whole molecule. The angles of the C(10), C(21), and C(32) triangle are 40.0, 68.4, and 71.8°, respectively; i.e., it is roughly isosceles. This is consistent with the fact that two of the ethyl groups are oriented toward the metal and one is not.

In $(C_5Me_4{}^iPr)_3La$, **12**, there are fewer options for orienting the R groups since each R contains two methyl groups. It is not possible to point one methyl directly toward or away from the metal without causing some unfavorable interactions between the other isopropyl methyl and the other ring methyls of the $C_5Me_4{}^iPr$ ring. There are no small displacements from the cyclopentadienyl plane of the isopropyl carbon atoms bound to the ring. These three carbon atoms, C(10), C(22), and C(34), again define a roughly isosceles triangle like that in **11** with angles of 41.5, 67.9, and 70.6°, respectively, but the closest contact between an isopropyl methyl group and the metal is C(23) at 4.01 Å. This C(23) is along the pseudo-C_3 axis of the molecule as was found for C(22) and C(11) in **11** (Figure 5). The next closest methyl carbons in **12**, C(35) and C(11), are 4.10 and 4.26 Å from La, respectively, and neither is directly along the pseudo-C_3 axis. These two R groups are on the same side of the molecule, which may cause additional constraints on their positions.

The structure of $(C_5Me_4SiMe_3)_3La$ shares features with both **11** and **12**. With the $SiMe_3$ group, there are even more constraints on R group orientation. Two of the $SiMe_3$ groups have one methyl carbon pointing in: C(24) on Si(2) and C(35) on Si(3) (Figure 5). This is the sterically most favorable orientation since two of the three methyls are pointed to the outside of the molecule where there is more space. However, the Si(1) group is on the same side of the molecule as the Si(2) group and has two of its methyl atoms pointed in, C(10) and C(11). Si(1) is also the silicon with the largest out of cyclopentadienyl ring plane displacement: 0.498 Å. The three substituent Si atoms define a distorted isosceles triangle with angles of 39.3, 67.9, and 72.9° as in the other structures. Only one methyl group is within 4 Å of the metal center: C(24) is 3.42 Å from the metal and lies on the pseudo-C_3 axis like the methyls in **11**. C(35) is close to the pseudo-C_3 axis, but it is 4.10 Å from La. In contrast to complex **12**, the R group with the closest methyl is on the same side of the molecule as another R group.

Ligand Exchange between 10 and 13. Since the diamagnetic nature of complexes **10**−**13** makes them more suitable for NMR studies than their paramagnetic analogues, a ligand exchange study could be performed with this series of compounds, as shown in Figure 6 in Supporting Information.

The ^1H NMR spectrum of an approximately equimolar mixture of **10** and **13** in benzene showed no immediate interchange of the ligands: only the 1.997 ppm resonance of **10** and the 2.36, 2.01, and 0.36 ppm shifts of **13** were observed. After 24 h, two new sets of four peaks were observed, set **A** (2.31, 2.02, 1.93, 0.31 ppm) and set **B** (2.33, 2.05, 1.98, 0.33 ppm), along with the original four peaks of the starting materials. After 92 h, only 5% of **10** and 10% of **13** remained and the ratio of a corresponding peak in **A** and **B** was 3.1:1 (for the 2.35 and 2.34 ppm resonances). These results are consistent with a ligand redistribution between $(C_5Me_5)_3La$ and $(C_5Me_4SiMe_3)_3$-La to form $(C_5Me_4SiMe_3)_2La(C_5Me_5)$ (**A**) and $(C_5Me_4SiMe_3)$-$La(C_5Me_5)_2$ (**B**) in a molar ratio of 1.6:1.

Discussion

The synthetic route involving reaction of an unsolvated cation $[(C_5Me_4R)_2La][BPh_4]$, with KC_5R_5, which was used to make $(C_5Me_5)_3Nd$ and $(C_5Me_5)_3Sm$,[5] can be extended to the largest lanthanide metal, lanthanum, as well as to substituted cyclopentadienyl ligands, C_5Me_4R where R = Et, ^{i}Pr, and $SiMe_3$. However, the synthesis of the less crowded $(C_5Me_5)_3La$ requires the use of silylated glassware to obtain the complex in pure crystalline form. It is unclear why the least sterically crowded example of the $(C_5Me_5)_3La$ series requires these more stringent reaction conditions. It suggests that the larger metal provides reaction pathways with oxygen-containing contaminants that are not available to the more crowded systems. Given this surprising reactivity, it is prudent to use silylated glassware, at least initially, when other highly reactive examples of $(C_5Me_5)_3M$ complexes are pursued synthetically.

The structures of the $(C_5Me_4R)_3La$ complexes do not show a large change in bonding parameters as the size of the R group is increased. Evidently, the presence of just a single substituent larger than methyl on each ring is not sufficient to significantly increase the overall crowding in the molecule. Apparently there is room for each R group to avoid the other R groups and the other ring methyls.

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The R = Et complex, $(C_5Me_4Et)_3La$, **11**, demonstrates this point most clearly. One ethyl group is oriented such that its end methyl group is away from the center of the molecule and the cyclopentadienyl ring. This orientation clearly will not affect the amount of steric crowding in the other parts of the molecule. Moreover, the remainder of the molecule is not too crowded to accommodate orienting the other ethyl groups *toward* the center of the molecule, presumably to access additional long distance metal ligand interaction.

In the case of R = ^iPr, $(C_5Me_4{}^iPr)_3La$, **12**, the presence of two methyl groups on each R does not allow the simple options taken in the R = Et complex. If one methyl is oriented directly in toward the metal on the pseudo-C_3 axis, it will cause some (isopropyl methyl)−(ring methyl) interactions, and this orientation is not observed. Instead, each isopropyl group appears to be oriented such that the hydrogen of the methine carbon is in the plane of the ring. This would put the smallest substituent on the methine carbon in the sterically most congested region as expected. This orientation leaves one methyl pointing in and one methyl pointing out from the cyclopentadienyl ring plane with each oriented at an angle consistent with a sp^3 hybridization around the methine carbon. As a result, none of the methyl positions can tip in toward the metal and there are no especially small out of plane displacements for the methine carbons. Complex **12** has three isopropyl methyl groups on the outside of the molecule, and the other three apparently can be accommodated without increasing the overall metal−ring centroid distances.

In the R = $SiMe_3$ case, $(C_5Me_4SiMe_3)_3La$, **13**, in which the R group contains three methyl groups, it is very difficult to avoid some Me(R)−Me(ring) interactions. However, since silicon−carbon bonds are longer than carbon−carbon bonds, each of these methyl groups can be oriented further away from the ring methyls. Hence, in **13**, one of the methyls can make a long-range La···Me interaction less than 4 Å despite the fact that its silicon has two other methyl groups. Interestingly, this occurs on the side of the molecule that has two $SiMe_3$ groups attached to it. Hence, even with the $SiMe_3$ substituent, the extra steric bulk can be accommodated.

Another aspect of the apparent ability of these $(C_5Me_4R)_3La$ systems to accommodate increased steric bulk is that they can exchange ligands. Although this process is kinetically slow between the smallest and largest complexes, **10** and **13**, it does occur to form mixed ligand species.

Conclusion

The results of this study show that a variety of $(C_5Me_4R)_3La$ complexes can be isolated and fully characterized with R groups as large as $SiMe_3$. The availability of these complexes in good yield, along with their diamagnetism, will facilitate the future reactivity investigations of sterically crowded tris(peralkylcyclopentadienyl) lanthanide complexes. Variation of ligand size should be especially useful for the evaluation of sterically induced reductions. In addition, the option to make tris(peralkylcyclopentadienyl) complexes with R groups that can block the approach of substrates to the metal along the pseudo-C_3 axes may be useful with the mechanistic investigations of these complexes.

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Supporting Information Available: Four X-ray crystallographic files, in CIF format, and representative ^1H NMR spectra for the exchange reaction of **10** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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