cant of only 19.1°, while this angle for its cobalt complex[26] is 44°, a considerably greater difference than that between the unprotonated free base and its complex.

Metalloporphyrins other than heme are able to bind to heme oxygenase, and zinc complexes act as competitive inhibitors of this enzyme. When De Matteis and co-workers tested the inhibitory ability of a series of zinc *N*-alkylporphyrin complexes, larger N-substituents (ethyl and propyl) were found to be less inhibitory than *N*-methylporphyrins.[3] They proposed that the correlation between structure and inhibition for this enzyme was also related to the cant of the N-substituted pyrrole ring, with larger groups causing a greater tilt. While there are, indeed, substantial differences in the cant of the N-substituted pyrrole ring among the members of the series of N-substituted zinc(II) porphyrins reported herein, these differences are not straightforwardly related to the "bulk" of the N-substituent. In fact, the pyrrole ring for which the N-substituent is a benzyl group is less canted (by 7°) than in the complex with a methyl substituent. In the series of *N*-alkylporphyrins studied by DeMatteis, the N-substituents are very similar (*N*-methyl-, *N*-ethyl-, and *N*-*n*-propyl groups), all involving an *N*-methylene linkage. No substantial difference in the cant of the pyrrole ring is expected for these compounds. On the basis of our results, the differences in heme oxygenase inhibition for the zinc(II) complexes of *N*-alkylprotoporphyrin are due not to the cant of the N-substituted pyrrole ring but instead to the requirement for additional space in the binding pocket to accommodate more bulky N-substituents. The need to accommodate the N-substituent also explains the marked difference in inhibition of ferrochelatase by *N*-*n*-propylprotoporphyrin IX and *N*-*n*-propylmesoporphyrin IX in comparison with the corresponding *N*-methyl and *N*-ethyl free base porphyrins.

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Supplementary Material Available: Table S-1, anisotropic thermal parameters for [Zn(*N*-Bz-TPP)Cl], Table S-II, calculated hydrogen atom coordinates for [Zn(*N*-Bz-TPP)Cl], Table S-III, least-squares planes for [Zn(*N*-Bz-TPP)Cl], Table S-V, anisotropic thermal parameters for [Zn(*N*-Ph-TPP)Cl], Table S-VI, calculated hydrogen atom coordinates for [Zn(*N*-Ph-TPP)Cl], and Table S-VII, least-squares planes for [Zn(*N*-Ph-TPP)Cl] (14 pages); Table S-IV, observed and calculated structure factors for [Zn(*N*-Bz-TPP)Cl], and Table S-VIII, observed and calculated structure factors for [Zn(*N*-Ph-TPP)Cl] (57 pages). Ordering information is given on any current masthead page.

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Structural Diversity in Bis(pentamethylcyclopentadienyl)lanthanide Halide Complexes: X-ray Crystal Structures of $[(C_5Me_5)_2SmCl]_3$ and $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$

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Abstract: $(C_5Me_5)_2SmCl$ (THF) can be desolvated at 150 °C to form a material which crystallizes from hexane/toluene as the cyclic trimer $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ in space group $C2/c$ with $a = 21.665$ (10) Å, $b = 14.203$ (8) Å, $c = 20.234$ (8) Å, $\beta = 108.63$ (6)°, $V = 5900$ Å^3, and $D_{calcd} = 1.54$ g cm^{-3} for $Z = 4$ (four trimetallic units per unit cell). The three bridging chloride ions connect the three $(C_5Me_5)_2Sm$ units via 2.849 (7)–2.892 (7) Å Sm–(μ-Cl) distances in a planar six-membered $Sm_3(\mu\text{-}Cl)_3$ ring. In the presence of tetraglyme, crystals of $\{(C_5Me_5)_2ClSm(\mu\text{-}Cl)Sm(C_5Me_5)_2[\mu,\eta^4\text{-}CH_3(OCH_2CH_2)_4OCH_3]Sm(C_5Me_5)_2\}^+\{[(C_5Me_5)_2ClSm]_2(\mu\text{-}Cl)\}^-$ form in space group $P2_1/a$ with $a = 19.185$ (8) Å, $b = 26.627$ (9) Å, $c = 24.760$ (9) Å, $\beta = 115.16$ (5)°, $V = 11\,448.3$ Å^3, and $D_{calcd} = 1.45$ g cm^{-3} for $Z = 4$ (four pentametallic units per unit cell). The structure contains four independent types of $(C_5Me_5)_2Sm$ units and a variety of Sm–Cl bonds. This allows a detailed analysis of trends in structural preferences, bond distances, and angles.

Recent studies of the chemistry of organolanthanide alkyl and hydride complexes have shown that reactivity can be highly dependent on the structure of the complex.[2-7] Hence, the degree of steric saturation around the metal, the presence of terminal vs. bridging ligands, and the degree of oligomerization of the complex can strongly influence how a Ln–CR_3 or Ln–H unit reacts (Ln = lanthanide metal).[2] As a consequence, defining the

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Table I. Crystallographically Defined Bis(cyclopentadienyl) Derivatives of Trivalent Lanthanides

halide derivatives characterized by X-ray crystallography	alkyl or hydride analogues characterized by X-ray crystallography
Bridged Dimers	
$[(C_5H_5)_2Sc(\mu\text{-}Cl)]_2$[15] $[(CH_3C_5H_4)_2Yb(\mu\text{-}Cl)]_2$[16] $\{[C_5H_3(SiMe_3)_2]_2Ln(\mu\text{-}Cl)\}_2$[17] (Ln = Pr, Sc, Yb) $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$[14]	$[(C_5H_5)_2Ln(\mu\text{-}CH_3)]$[11] (Ln = Yb, Y) $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}CH_3)]_2$[19] $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$[9] (hydrogens not located)
Solvated Bridged Dimers	
$[(C_5H_5)_2(THF)Nd(\mu\text{-}Cl)]_2$[20]	$[(CH_3C_5H_4)_2(THF)Ln(\mu\text{-}H)]_2$[8] (Ln = Y, Er) $[(1,3\text{-}Me_2C_5H_3)_2(THF)Y(\mu\text{-}H)]_2$[19]
Heterometallic Bridged Species	
$(C_5Me_5)_2Yb(\mu\text{-}X)_2Li(Et_2O)_2$[21] (X = Cl, I) $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(DME)_2$[22] $(C_5H_4SiPh_2Me)_2Yb(\mu\text{-}Cl)_2Li(Et_2O)_2$[21] $[C_5H_3(SiMe_3)_2]_2Nd(\mu\text{-}Cl)_2Li(THF)_2$[23] $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2AlCl_2$[21] $[Me_2Si(C_5Me_4)_2Nd]_2(\mu\text{-}Cl)_3Li(THF)_2$[24]	$(C_5H_5)_2Ln(\mu\text{-}Me)_2Li(TMEDA)$[25] (Ln = Lu, Er) $(C_5H_5)_2Yb(\mu\text{-}Me)_2AlMe_2$[26]
Monomers	
$(C_5H_5)_2LnCl(THF)$[27] $(C_5Me_5)_2LnX(THF)$[28] (Ln = Sm, X = I, Cl) (Ln = Y, X = Cl) $\{[C_5H_3(SiMe_3)_2]_2NdCl_2\}\{AsPh_4\}$[29]	$(C_5Me_5)_2Sm(C_6H_5)(THF)$[30] $(C_5H_5)_2LuR(THF)$ (R = $t\text{-}C_4H_9$,[31] CH_2SiMe_3,[32] C_6H_4Me[3]) $(C_5H_5)_2Yb(CH_3)(THF)$[5] $[(C_5H_5)_2Y(CH_2SiMe_3)_2]_2Li_2(C_4H_8O_2)(MeOCH_2CH_2OMe)$[33] $(C_5Me_5)_2NdCH(SiMe_3)_2$[34]
Trimers	
$\{[(C_5H_5)_2Er(\mu\text{-}Cl)][(C_5H_5)_2Er(\mu\text{-}H)]_2(\mu_3\text{-}H)\}\{Li(THF)_4\}$[35]	$\{[(C_5H_5)_2Lu(\mu\text{-}H)]_3(\mu_3\text{-}H)\}\{Li(THF)_4\}$ (hydrogens not located)[35] $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$ (hydrogens not located)[19]

structural trends of organolanthanide complexes is crucial to understanding the chemistry of these compounds.

X-ray crystallography provides solid-state information on general structural patterns, but unfortunately the isolation of X-ray quality crystals of the often highly reactive alkyl and hydride complexes can be difficult. Even when good crystals are available, location of a hydride ligand in the presence of a heavy metal may be difficult,[8,9] and ambiguities in alkyl bonding can arise. For example, bridging methyl groups can bond via metal–carbon or via metal–hydrogen interactions.[10,11]

Historically, lanthanide halide analogues of organolanthanide hydride and alkyl complexes have proven useful in defining structural trends.[12-14] The generally less reactive halide analogues are not as difficult to isolate in high quality crystalline form, and the location of the halide ligand can be specified more precisely. For trivalent bis(cyclopentadienyl)lanthanide complexes $[(C_5R_5)_2LnZ]_n$ (R = H, Me; Z = halide, hydride, alkyl; n = 1–3), more structural information is available for the halide derivatives than for the hydride or alkyl complexes as shown in Table I.[15-35]

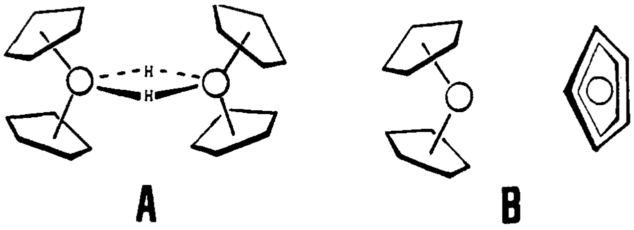

Figure 1. (A) Bent metallocene view of a $(C_5R_5)_2M(\mu\text{-}H)_2M(C_5R_5)_2$ molecule. (B) Structure observed in $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$.

Since our discovery and X-ray crystal study of the bis(cyclopentadienyl)samarium hydride, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$,[9] we have

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been interested in examining the formally analogous halide complex "$[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_2$". The hydride complex had an unusual structure which was not that predicted for a normal transition-metal bent metallocene[36] and which did not match the lowest energy structure predicted by a molecular orbital analysis of $[(C_5H_5)_2SmH]_2$.[37] A typical bent metallocene dimer would contain a planar $Sm_2(\mu\text{-}H)_2$ unit which would bisect the (ring centroid)–metal–(ring centroid) angle of each $(C_5Me_5)_2Sm$ group. In this case, as shown in Figure 1A, the four C_5Me_5 ring centroids would describe a square-planar geometry. In the observed structure, Figure 1B, the four C_5Me_5 ring centroids define a tetrahedron, i.e., one $(C_5Me_5)_2Sm$ unit has twisted 90° with respect to the other. In this geometry, it is impossible for a $Sm_2(\mu\text{-}H)_2$ plane to simultaneously bisect the (ring centroid)–metal–(ring centroid) angles of each $(C_5Me_5)_2Sm$ unit. Unfortunately, in the hydride structure, the hydrogen atoms could not be located.[9]

By studying the $(C_5Me_5)_2SmCl$ system we sought to determine if the chloride analogue (a) would be structurally similar to the hydride, (b) would adopt the bent metallocene structure due to the larger size of the chloride ligands vs. the hydrides, or (c) would adopt a different geometry. In this report, we describe the synthesis and crystallographic characterization of two bis(pentamethylcyclopentadienyl)samarium chloride systems which follow option c above. These complexes define new structural classes of bis(cyclopentadienyl)lanthanide halides and show that *several* different types of coordination geometry are available to a single set of ligands in a crystalline organolanthanide complex.

Experimental Section

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

Materials. Hexane was washed with sulfuric acid, dried over $MgSO_4$, and distilled from potassium benzophenone ketyl solubilized with tetraglyme. Toluene and THF were distilled from potassium benzophenone ketyl. Benzene-d_6 and toluene-d_8 were vacuum transferred from potassium benzophenone ketyl. $(C_5Me_5)_2SmCl(THF)$ was prepared by reacting $t\text{-}C_4H_9Cl$ with $(C_5Me_5)_2Sm(THF)_2$ as previously described.[28]

$[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ (1). In a glovebox, $(C_5Me_5)_2SmCl(THF)$ (0.85 g, 1.6 mmol) was placed in a tube fitted with a high vacuum stopcock adapter. The tube was attached to a vacuum line, and the sample was heated for 36 h at 90 °C under dynamic vacuum at about 10^{-5} torr. The originally orange sample turned orange-red during this time. The tube was removed from the vacuum line and taken into a glovebox containing no ether solvents. The sample was removed from the tube (0.61 g, 83%) and found to be pure by ^1H NMR spectroscopy, which showed a single C_5Me_5 resonance. Anal. Calcd for $Sm_3C_{60}H_{90}Cl_3$: Sm, 33.0. Found: Sm, 32.1; ^1H NMR (C_6D_6) δ −0.22 (s, C_5Me_5). The ^1H NMR shift is highly sensitive to traces of THF. Opening an NMR tube containing the sample for 1 min in a glovebox containing some THF vapor can cause a downfield shift of as much as 0.04 ppm. NMR samples which retained the red color of unsolvated **1** (vs. the orange color of $(C_5Me_5)_2SmCl(THF)$[28]) have exhibited the C_5Me_5 resonance at shifts as positive as δ 0.23 (cf. δ 1.20 for fully solvated $(C_5Me_5)_2SmCl(THF)$[28]): IR (KBr) 2850 w, 2400 w, 1440 m br, 1250 w, 1130 w, 1010 m br, 790 m cm^{-1}. X-ray quality crystals of $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ were grown at room temperature by layering hexane onto a saturated toluene solution made by dissolving the sample in hot toluene.

$(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$ (2). $(C_5Me_5)_2SmCl(THF)$ was desolvated as described above at 150 °C over a 1-h period. During this time the pressure rose from 10^{-5} to $>10^{-3}$ torr and then dropped back to 10^{-5} torr. The remaining pink powder was heated to 175 °C for 30 min, and the tube was sealed. The material was sublimed at 165 °C over a 3-day period to give red needles which were not, however, X-ray quality. (A sample of the crystals in THF-d_8 gave a clean ^1H NMR spectrum characteristic of $(C_5Me_5)_2SmCl(THF)$.) A sample of the sublimed crystals was stirred in toluene, and the resulting solution was decanted into a vial. Hexane containing a trace of tetraglyme was layered over the toluene, and the vial was loosely capped. After the solvent evaporated from the vial, crystals of $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$ remained.

Table II. Crystal Data for $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ (**1**) and $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$ (**2**)

	1	**2**
compd	$Sm_3Cl_3C_{60}H_{90}$	$Sm_5Cl_5C_{110}H_{172}O_5$
mol wt	1368.80	2503.65
space group	$C2/c$	$P2_1/a$
cell constants		
a, Å	21.665 (10)	19.185 (8)
b, Å	14.203 (8)	26.627 (9)
c, Å	20.234 (8)	24.760 (9)
α, deg	90.00	90.00
β, deg	108.63 (6)	115.16 (5)
γ, deg	90.00	90.00
cell vol, Å	5900.06	11448.3
molecules/unit cell	4 trimetallic units	4 pentametallic units
ρ(calcd), g cm^{-3}	1.54	1.45
μ (calcd), cm^{-1}	31.69	27.24
radiation	Mo Kα	Mo Kα
max/crystal/dimens, mm	0.15 × 0.20 × 0.15	0.15 × 0.25 × 0.10
scan width, deg	$0.8 + 0.2 \tan \theta$	$0.8 + 0.2 \tan \theta$
stnd reflctns	930, 008, 440	400, 040, 006
decay of stnds	±2%	±2%
reflctns measured	5315	8954
2θ range	2–36°	2–36°
obsd reflctns	1400	5218
no. of parameters varied	149	626
GOF	1.23	1.55
R	0.053	0.087
R_w	0.059	0.089

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ (1) and $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$ (2). Single crystals of the air-sensitive compounds were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 reflections ($2\theta > 20°$) accurately centered on the diffractometer are given in Table II. Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique as previously described.[26] Summaries of data collection parameters are given in Table II. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.[38]

Systematic absences indicated that the space group for **1** could be Cc or $C2/c$. Subsequent solution and refinement of the structure showed $C2/c$ to be the correct choice. The two crystallographically independent samarium atoms were located with the aid of MULTAN 80.[39] The calculation of difference Fourier maps allowed the location of the remaining non-hydrogen atoms. Neutral atom scattering factors for Sm, Cl, and C were taken from Cromer and Waber.[40] The full-matrix least-squares refinement (using the SHELX program system[41]) with isotropic temperature factors for all non-hydrogen atoms led to a reliability index $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.095$. Conversion to anisotropic thermal parameters for Sm and Cl atoms and further refinement gave $R = 0.053$ based on 1400 observed reflections ($(I) > 3\sigma(I)$). The function minimized in the least-squares calculation was $\sum w|\Delta F^2|$ with unit weights. In the last stage of refinement no parameter shifted by more than 0.01 of its estimated standard deviation. A final difference Fourier synthesis showed no unaccounted electron density. No systematic variation of $\omega(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters for **1** are given in Table III.

For complex **2**, the space group was uniquely determined to be $P2_1/a$ (an alternate setting of $P2_1/c$) from systematic absences. Solution refinement was carried out as described for **1**. MULTAN 80 was again used to locate the independent samarium positions. With isotropic temperature factors for all non-hydrogen atoms, $R = 0.114$. With anisotropic thermal parameters for the Sm and Cl atoms, $R = 0.087$. Final fractional coordinates for **2** are given in Table IV.

Results

Synthesis. Bis(pentamethylcyclopentadienyl)samarium chloride complexes can be made by reacting 2 equiv of MC_5Me_5 (M =

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Table III. Final Fractional Coordinates for $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$

atom	x/a	y/b	z/c
Sm(1)	0.87713 (6)	−0.0416 (1)	0.14647 (7)
Sm(2)	1.0000	−0.3856 (1)	0.2500
Cl(3)	0.9175 (3)	−0.2313 (5)	0.1805 (3)
Cl(4)	1.0000	0.0041 (7)	0.2500
Cp(5)	0.765 (1)	−0.063 (2)	0.176 (1)
Cp(6)	0.812 (1)	−0.042 (2)	0.241 (1)
Cp(7)	0.829 (1)	0.053 (2)	0.238 (1)
Cp(8)	0.794 (1)	0.090 (2)	0.170 (1)
Cp(9)	0.754 (1)	0.015 (2)	0.133 (1)
Cp(10)	0.850 (1)	0.049 (2)	0.019 (1)
Cp(11)	0.833 (1)	−0.045 (2)	0.001 (1)
Cp(12)	0.892 (1)	−0.099 (2)	0.023 (1)
Cp(13)	0.943 (1)	−0.033 (2)	0.056 (1)
Cp(14)	0.915 (1)	0.056 (2)	0.054 (1)
Cp(15)	0.940 (1)	−0.386 (2)	0.349 (1)
Cp(16)	0.892 (1)	−0.420 (2)	0.289 (1)
Cp(17)	0.910 (1)	−0.508 (2)	0.272 (1)
Cp(18)	0.969 (1)	−0.534 (2)	0.322 (1)
Cp(19)	0.988 (1)	−0.462 (2)	0.370 (1)
Me(20)	0.728 (1)	−0.159 (2)	0.157 (1)
Me(21)	0.833 (1)	−0.108 (2)	0.305 (1)
Me(22)	0.871 (1)	0.114 (2)	0.298 (1)
Me(23)	0.792 (1)	0.195 (2)	0.150 (1)
Me(24)	0.692 (1)	0.027 (2)	0.066 (1)
Me(25)	0.804 (1)	0.137 (2)	−0.010 (1)
Me(26)	0.766 (1)	−0.085 (2)	−0.045 (2)
Me(27)	0.896 (1)	−0.203 (2)	0.004 (1)
Me(28)	1.017 (1)	−0.059 (2)	0.084 (1)
Me(29)	0.954 (1)	0.145 (2)	0.078 (1)
Me(30)	0.936 (1)	−0.297 (2)	0.388 (1)
Me(31)	0.826 (1)	−0.372 (2)	0.247 (1)
Me(32)	0.866 (1)	−0.574 (2)	0.215 (2)
Me(33)	0.999 (2)	−0.631 (3)	0.335 (2)
Me(34)	1.050 (1)	−0.451 (2)	0.436 (1)

alkali metal) with $SmCl_3$ in THF[28,42] or by oxidizing $(C_5Me_5)_2Sm(THF)_2$ with an alkyl chloride.[28] Since the first route forms MCl adducts $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2ML_2$ (L_2 = $(THF)_2$, $(Et_2O)_2$, or TMEDA) as the predominant product, the second synthesis is preferred. The $(C_5Me_5)_2SmCl(THF)$ product obtained must be desolvated to get a complex with the desired empirical formula "$(C_5Me_5)_2SmCl$".

Powdered $(C_5Me_5)_2SmCl(THF)$ can be desolvated under high vacuum at temperatures ranging from 90 to 150 °C. The sample becomes orange-red upon desolvation. Sublimation occurs very slowly at 165 °C or more rapidly at 200 °C and can give red crystals. The desolvated material is insoluble in hexane, sparingly soluble in benzene and toluene, and more soluble in boiling toluene. The sublimed material has a single broad ($w_{1/2}$ = 9.7 Hz) C_5Me_5 resonance at −0.22 ppm in the ^1H NMR spectrum. The position of the peak is very sensitive to trace amounts of THF. Exposure of an NMR sample in the tube to THF vapor moves the resonance downfield. Addition of a full equivalent of THF-d_8 to the NMR sample sharpens and shifts the resonance downfield to 1.2 ppm, which is characteristic of the original solvate.[28] Samples of the powdered, desolvated material which have not been sublimed typically have their C_5Me_5 resonance at 0.07–0.23, and traces of coordinated THF are sometimes detected around −0.3 and −1.4 ppm.

Although sublimation yielded single crystals, none of those examined diffracted well enough for a structural determination. X-ray quality crystals of $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$, **1**, were successfully obtained by diffusion of hexane into a saturated toluene solution of desolvated material. Crystals of $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$, **2**, were obtained when hexane containing a trace of tetraglyme was layered over a more dilute solution of the sublimed material in toluene.

Structure of $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$. In the absence of any coordinating ether, $(C_5Me_5)_2SmCl$ units crystallize into trimeric molecular species as shown in Figure 2. The $Sm_3(\mu\text{-}Cl)_3$ unit is exactly planar and has approximate C_{2v} symmetry with Sm(2) and Cl(4) on the C_2 axis. Inspection of the three independent Sm–Cl distances, 2.849 (7), 2.892 (7), and 2.887 (3) Å, the two Cl–Sm–Cl angles, 81.5 (2)° and 84.0 (2)°, and the two Sm–Cl–Sm angles, 154.0 (3)° and 158.2(3)° (Table V), shows that the $Sm_3(\mu\text{-}Cl)_3$ unit has nearly D_{3h} symmetry. The pairs of C_5Me_5 rings associated with each samarium atom have a staggered orientation with (ring a carbon)–(centroid a)–(centroid b)–(ring b carbon) torsional angles in the 35–47° range.

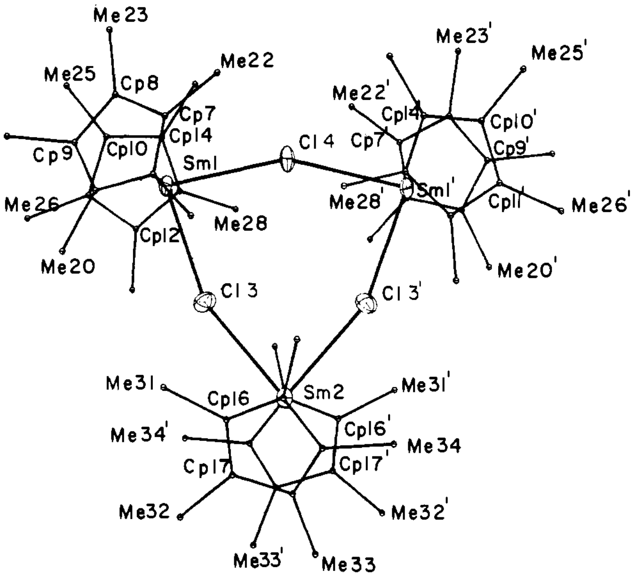

Figure 2. Molecular structure of $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ (**1**). Carbon atoms have been reduced to dots for clarity.

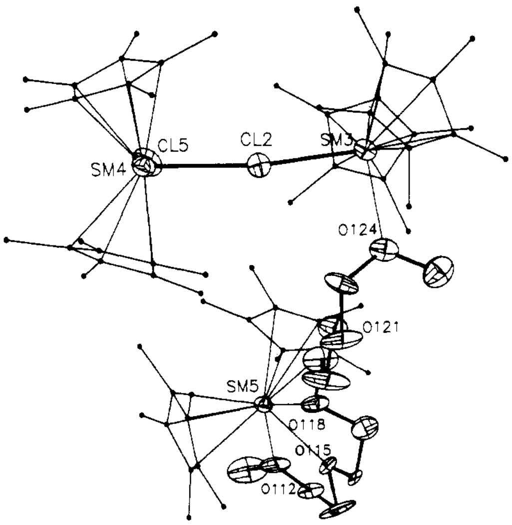

Figure 3. Structure of the $\{(C_5Me_5)_2ClSm(\mu\text{-}Cl)Sm(C_5Me_5)_2[\mu,\eta^4\text{-}Me(OCH_2CH_2)_4OMe]Sm(C_5Me_5)_2\}^+$ cation. C_5Me_5 carbon atoms are shown as dots for clarity.

Structure of $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$. In the presence of a trace amount of tetraglyme, $(C_5Me_5)_2SmCl$ units crystallize from toluene in a complex structure which has four different Sm^{3+} coordination environments. These can be described by the detailed formula $\{(C_5Me_5)_2ClSm(\mu\text{-}Cl)Sm(C_5Me_5)_2[\mu,\eta^4\text{-}Me(OCH_2CH_2)_4OMe]Sm(C_5Me_5)_2\}^+\{[(C_5Me_5)_2ClSm]_2(\mu\text{-}Cl)\}^-$. The cation, shown in Figure 3, contains a $[(C_5Me_5)_2Sm]^+$ unit ligated by three oxygen atoms of the tetraglyme molecule along with a neutral $(C_5Me_5)_2ClSm(\mu\text{-}Cl)Sm(C_5Me_5)_2$ unit attached to another oxygen atom of the tetraglyme. The remaining oxygen atom in tetraglyme is not coordinated to a metal atom.

The anion in this system, shown in Figure 4, is like the neutral $(C_5Me_5)_2ClSm(\mu\text{-}Cl)Sm(C_5Me_5)_2$–O(tetraglyme) unit in the cation except that a terminal chloride ligand replaces the tetraglyme oxygen atom. In each of these bimetallic samarium units

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(42) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267–3270.

Table IV. Final Fractional Coordinates for $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Sm(1)	0.4036 (1)	0.305 60 (7)	0.548 96 (9)	Me(34)	0.452 (2)	0.495 (2)	0.576 (2)
Sm(2)	0.2628 (1)	0.477 85 (7)	0.572 43 (9)	Me(35)	0.453 (2)	−0.567 (2)	1.690 (2)
Sm(3)	0.3873 (1)	0.248 07 (8)	1.174 00 (9)	Cp(41)	0.232 (2)	0.248 (2)	1.111 (2)
Sm(4)	0.3381 (1)	0.361 21 (8)	0.9698 (1)	Cp(42)	0.250 (2)	0.289 (1)	1.148 (2)
Sm(5)	1.1403 (1)	0.559 55 (7)	1.212 79 (9)	Cp(43)	0.271 (2)	0.277 (1)	1.205 (2)
Cl(1)	0.3180 (5)	0.3844 (3)	0.5613 (5)	Cp(44)	0.278 (2)	0.223 (2)	1.211 (2)
Cl(2)	0.3842 (5)	0.3067 (4)	1.0805 (4)	Cp(45)	0.249 (2)	0.210 (1)	1.153 (2)
Cl(3)	0.5389 (5)	0.3479 (4)	0.6060 (5)	Me(41)	0.198 (2)	0.249 (2)	1.042 (2)
Cl(4)	0.2486 (6)	0.5068 (4)	0.4659 (5)	Me(42)	0.235 (2)	0.343 (2)	1.124 (2)
Cl(5)	0.1979 (6)	0.3740 (4)	0.9584 (6)	Me(43)	0.288 (2)	0.311 (2)	1.261 (2)
C(111)	1.020 (3)	0.655 (2)	1.235 (3)	Me(44)	0.294 (2)	0.190 (1)	1.265 (2)
O(112)	1.088 (2)	0.624 (1)	1.263 (2)	Me(45)	0.229 (2)	0.151 (2)	1.126 (2)
C(113)	1.117 (4)	0.629 (2)	1.319 (2)	Cp(51)	0.449 (2)	0.155 (2)	1.202 (2)
C(114)	1.211 (4)	0.618 (2)	1.359 (2)	Cp(52)	0.504 (3)	0.187 (2)	1.252 (2)
O(115)	1.217 (2)	0.5771 (9)	1.320 (1)	Cp(53)	0.534 (2)	0.215 (2)	1.218 (2)
C(116)	1.299 (3)	0.562 (2)	1.355 (1)	Cp(54)	0.511 (2)	0.205 (2)	1.162 (2)
C(117)	1.300 (3)	0.510 (2)	1.335 (2)	Cp(55)	0.450 (2)	0.163 (1)	1.148 (2)
O(118)	1.279 (1)	0.512 (1)	1.268 (1)	Me(51)	0.414 (3)	0.106 (2)	1.216 (2)
C(119)	1.296 (3)	0.466 (2)	1.247 (2)	Me(52)	0.526 (3)	0.184 (2)	1.315 (3)
C(120)	1.387 (2)	0.467 (2)	1.265 (3)	Me(53)	0.602 (2)	0.255 (2)	1.249 (2)
O(121)	1.393 (1)	0.417 (1)	1.242 (1)	Me(54)	0.535 (2)	0.219 (2)	1.114 (2)
C(122)	1.474 (2)	0.412 (2)	1.258 (2)	Me(55)	0.406 (3)	0.134 (2)	1.091 (2)
C(123)	1.482 (2)	0.362 (2)	1.226 (2)	Cp(61)	0.334 (2)	0.267 (2)	0.933 (2)
O(124)	1.453 (1)	0.319 (1)	1.249 (1)	Cp(62)	0.262 (2)	0.288 (1)	0.886 (2)
C(125)	1.482 (3)	0.312 (2)	1.314 (2)	Cp(63)	0.285 (3)	0.327 (2)	0.860 (2)
Cp(01)	0.446 (2)	0.265 (1)	0.660 (2)	Cp(64)	0.364 (3)	0.329 (2)	0.876 (2)
Cp(02)	0.367 (2)	0.269 (1)	0.638 (1)	Cp(65)	0.398 (3)	0.291 (2)	0.921 (2)
Cp(03)	0.331 (2)	0.237 (1)	0.593 (2)	Me(61)	0.345 (2)	0.219 (1)	0.968 (2)
Cp(04)	0.387 (2)	0.211 (2)	0.581 (2)	Me(62)	0.183 (3)	0.267 (2)	0.879 (2)
Cp(05)	0.457 (2)	0.228 (2)	0.620 (2)	Me(63)	0.226 (3)	0.350 (2)	0.804 (3)
Me(01)	0.510 (3)	0.286 (2)	0.715 (2)	Me(64)	0.406 (3)	0.352 (2)	0.844 (3)
Me(02)	0.329 (2)	0.300 (2)	0.672 (2)	Me(65)	0.487 (3)	0.281 (2)	0.956 (2)
Me(03)	0.241 (3)	0.234 (2)	0.561 (2)	Cp(71)	0.454 (2)	0.424 (1)	1.038 (2)
Me(04)	0.370 (3)	0.166 (2)	0.540 (2)	Cp(72)	0.384 (2)	0.445 (1)	1.039 (2)
Me(05)	0.534 (3)	0.204 (2)	0.624 (2)	Cp(73)	0.338 (3)	0.461 (2)	0.979 (2)
Cp(11)	0.405 (2)	0.263 (2)	0.450 (2)	Cp(74)	0.381 (3)	0.455 (2)	0.948 (2)
Cp(12)	0.446 (2)	0.305 (2)	0.459 (2)	Cp(75)	0.448 (2)	0.435 (2)	0.982 (2)
Cp(13)	0.397 (3)	0.344 (2)	0.447 (2)	Me(71)	0.520 (3)	0.403 (2)	1.096 (2)
Cp(14)	0.326 (3)	0.329 (2)	0.435 (2)	Me(72)	0.363 (2)	0.445 (2)	1.093 (2)
Cp(15)	0.329 (3)	0.275 (2)	0.433 (2)	Me(73)	0.263 (3)	0.494 (2)	0.964 (2)
Me(11)	0.440 (3)	0.211 (2)	0.445 (2)	Me(74)	0.349 (3)	0.479 (2)	0.883 (2)
Me(12)	0.535 (3)	0.306 (2)	0.472 (2)	Me(75)	0.520 (3)	0.423 (2)	0.969 (2)
Me(13)	0.411 (3)	0.406 (2)	0.446 (2)	Cp(81)	1.072 (2)	0.471 (2)	1.165 (2)
Me(14)	0.247 (3)	0.358 (2)	0.408 (2)	Cp(82)	1.006 (2)	0.505 (1)	1.141 (2)
Me(15)	0.257 (2)	0.241 (2)	0.407 (2)	Cp(83)	1.001 (2)	0.521 (1)	1.198 (1)
Cp(21)	0.116 (3)	0.504 (2)	0.546 (2)	Cp(84)	1.062 (2)	0.490 (2)	1.246 (2)
Cp(22)	0.103 (3)	0.476 (2)	0.501 (3)	Cp(85)	1.098 (2)	0.461 (2)	1.221 (2)
Cp(23)	0.126 (2)	0.429 (2)	0.535 (2)	Me(81)	1.091 (2)	0.440 (2)	1.116 (2)
Cp(24)	0.153 (2)	0.440 (2)	0.605 (2)	Me(82)	0.956 (3)	0.516 (2)	1.078 (2)
Cp(25)	0.146 (2)	0.490 (2)	0.605 (2)	Me(83)	0.928 (2)	0.545 (2)	1.195 (2)
Me(21)	0.084 (3)	0.549 (2)	0.498 (3)	Me(84)	1.058 (3)	0.495 (2)	1.307 (3)
Me(22)	0.081 (5)	0.445 (3)	0.444 (4)	Me(85)	1.147 (3)	0.420 (2)	1.257 (2)
Me(23)	0.130 (3)	0.369 (2)	0.532 (3)	Cp(91)	1.104 (2)	0.628 (1)	1.121 (2)
Me(24)	0.181 (3)	0.407 (2)	0.661 (3)	Cp(92)	1.163 (3)	0.651 (2)	1.176 (2)
Me(25)	0.146 (3)	0.518 (2)	0.657 (2)	Cp(93)	1.224 (3)	0.632 (2)	1.183 (3)
Cp(31)	0.363 (2)	0.510 (2)	0.685 (2)	Cp(94)	1.212 (3)	0.592 (2)	1.144 (2)
Cp(32)	0.337 (2)	0.554 (2)	0.649 (2)	Cp(95)	1.141 (3)	0.587 (2)	1.110 (2)
Cp(33)	0.362 (2)	0.555 (1)	0.609 (2)	Me(91)	1.022 (3)	0.646 (2)	1.085 (3)
Cp(34)	0.411 (2)	0.508 (1)	0.613 (2)	Me(92)	1.152 (3)	0.701 (2)	1.203 (3)
Cp(35)	0.408 (2)	0.485 (2)	0.663 (2)	Me(93)	1.310 (5)	0.641 (3)	1.235 (4)
Me(31)	0.355 (3)	0.497 (2)	0.744 (2)	Me(94)	1.274 (4)	0.556 (3)	1.136 (3)
Me(32)	0.295 (3)	0.601 (2)	0.658 (2)	Me(95)	1.106 (3)	0.563 (2)	1.047 (3)
Me(33)	0.357 (2)	0.595 (2)	0.564 (2)				

the four C_5Me_5 ring centroids approximately describe a tetrahedron; i.e., the $(C_5Me_5)_2Sm$ units are twisted 90° with respect to each other. In the anion, the two planes defined by terminal Cl, metal, and bridging Cl have an approximately 90° angle between them. In the cation the two similar planes defined by terminal Cl, metal, and bridging Cl and by terminal O (from tetraglyme), metal, and bridging Cl are also approximately orthogonal.

Table VI presents selected metrical data on **2**. Full bond distance and bond angle data are given in the supplementary material.

Discussion

$[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ (**1**) represents the first trimeric bis(pentamethylcyclopentadienyl)lanthanide complex known. The most closely related system is the actinide compound $[(C_5Me_5)_2U(\mu\text{-}Cl)]_3$, whose structural parameters are compared in Table VII.[43] The only structurally characterized organolanthanide trimers available for comparison with **1** are [(1,3-

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[43] Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075–5078.

Table V. Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$

Distances			
Sm(1)–Cl(3)	2.849 (7)	Sm(1)–Cl(4)	2.887 (3)
Sm(1)–Cp(5)	2.69 (2)	Sm(1)–Cp(6)	2.72 (2)
Sm(1)–Cp(7)	2.74 (2)	Sm(1)–Cp(8)	2.74 (2)
Sm(1)–Cp(9)	2.72 (2)	Sm(1)–Cp(10)	2.78 (2)
Sm(1)–Cp(11)	2.79 (2)	Sm(1)–Cp(12)	2.74 (2)
Sm(1)–Cp(13)	2.66 (2)	Sm(1)–Cp(14)	2.66 (2)
Sm(2)–Cl(3)	2.892 (7)	Sm(2)–Cp(15)	2.71 (2)
Sm(2)–Cp(16)	2.73 (3)	Sm(2)–Cp(17)	2.75 (3)
Sm(2)–Cp(18)	2.78 (3)	Sm(2)–Cp(19)	2.75 (2)
Cp(5)–Cp(6)	1.42 (3)	Cp(5)–Cp(9)	1.38 (3)
Cp(5)–Me(20)	1.57 (4)	Cp(6)–Cp(7)	1.41 (4)
Cp(6)–Me(21)	1.53 (3)	Cp(7)–Cp(8)	1.44 (3)
Cp(7)–Me(22)	1.53 (3)	Cp(8)–Cp(9)	1.43 (3)
Cp(8)–Me(23)	1.54 (4)	Cp(9)–Me(24)	1.57 (3)
Cp(10)–Cp(11)	1.40 (3)	Cp(10)–Cp(14)	1.37 (3)
Cp(10)–Me(25)	1.59 (4)	Cp(11)–Cp(12)	1.43 (3)
Cp(11)–Me(26)	1.56 (3)	Cp(12)–Cp(13)	1.43 (3)
Cp(12)–Me(27)	1.54 (4)	Cp(13)–Cp(14)	1.40 (3)
Cp(13)–Me(28)	1.56 (3)	Cp(14)–Me(29)	1.51 (3)
Cp(15)–Cp(16)	1.42 (3)	Cp(15)–Cp(19)	1.46 (3)
Cp(15)–Me(30)	1.50 (4)	Cp(16)–Cp(17)	1.39 (3)
Cp(16)–Me(31)	1.56 (3)	Cp(17)–Cp(18)	1.40 (3)
Cp(17)–Me(32)	1.56 (4)	Cp(18)–Cp(19)	1.38 (3)
Cp(18)–Me(33)	1.51 (4)	Cp(19)–Me(34)	1.56 (3)
Sm(1)–Sm(1)′	5.625 (2)	Sm(1)–Sm(2)	5.637 (2)
Sm(1)–Cl(3)′	5.418 (7)	Sm(1)–Cn(1)	2.44
Sm(1)–Cn(2)[a]	2.45	Sm(2)–Cl(4)	5.53 (1)
Sm(2)–Cn(3)	2.47	Cl(3)–Cl(3)′	3.77 (1)
Cl(3)–Cl(4)	3.84 (1)		
Angles			
Cl(3)–Sm(1)–Cl(4)	84.0 (2)	Cl(3)–Sm(2)–Cl(3)′	81.5 (2)
Sm(1)–Cl(3)–Sm(2)	158.2 (3)	Sm(1)–Cl(4)–Sm(1)′	154.0 (3)
Cp(6)–Cp(5)–Cp(9)	111 (2)	Cp(6)–Cp(5)–Me(20)	125 (2)
Cp(9)–Cp(5)–Me(20)	124 (2)	Cp(5)–Cp(6)–Cp(7)	106 (2)
Cp(5)–Cp(6)–Me(21)	126 (2)	Cp(7)–Cp(6)–Me(21)	128 (2)
Cp(6)–Cp(7)–Cp(8)	109 (2)	Cp(6)–Cp(7)–Me(22)	127 (2)
Cp(8)–Cp(7)–Me(22)	123 (2)	Cp(7)–Cp(8)–Cp(9)	106 (2)
Cp(7)–Cp(8)–Me(23)	124 (2)	Cp(9)–Cp(8)–Me(23)	129 (2)
Cp(5)–Cp(9)–Cp(8)	108 (2)	Cp(5)–Cp(9)–Me(24)	125 (2)
Cp(8)–Cp(9)–Me(24)	125 (2)	Cp(11)–Cp(10)–Cp(14)	110 (2)
Cp(11)–Cp(10)–Me(25)	126 (2)	Cp(14)–Cp(10)–Me(25)	124 (2)
Cp(10)–Cp(11)–Cp(12)	108 (2)	Cp(10)–Cp(11)–Me(26)	127 (2)
Cp(12)–Cp(11)–Me(26)	124 (2)	Cp(11)–Cp(12)–Cp(13)	106 (2)
Cp(11)–Cp(12)–Me(27)	124 (2)	Cp(13)–Cp(12)–Me(27)	130 (2)
Cp(12)–Cp(13)–Cp(14)	108 (2)	Cp(12)–Cp(13)–Me(28)	124 (2)
Cp(14)–Cp(13)–Me(28)	127 (2)	Cp(10)–Cp(14)–Cp(13)	108 (2)
Cp(10)–Cp(14)–Me(29)	127 (2)	Cp(13)–Cp(14)–Me(29)	124 (2)
Cp(16)–Cp(15)–Cp(19)	105 (2)	Cp(16)–Cp(15)–Me(30)	125 (2)
Cp(19)–Cp(15)–Me(30)	129 (2)	Cp(15)–Cp(16)–Cp(17)	109 (2)
Cp(15)–Cp(16)–Me(31)	128 (2)	Cp(17)–Cp(16)–Me(31)	122 (2)
Cp(16)–Cp(17)–Cp(18)	109 (3)	Cp(16)–Cp(17)–Me(32)	125 (3)
Cp(18)–Cp(17)–Me(32)	125 (3)	Cp(17)–Cp(18)–Cp(19)	108 (3)
Cp(17)–Cp(18)–Me(33)	128 (3)	Cp(19)–Cp(18)–Me(33)	122 (3)
Cp(15)–Cp(19)–Cp(18)	109 (2)	Cp(15)–Cp(19)–Me(34)	120 (3)
Cp(18)–Cp(19)–Me(34)	131 (3)	Cl(4)–Sm(1)–Cn(1)	107.4
Cl(3)–Sm(1)–Cn(1)	114.2	Cl(3)–Sm(1)–Cn(2)	105.4
Cn(1)–Sm(1)–Cn(2)	128.2	Cl(3)–Sm(1)–Cl(4)	84.0 (2)
Cl(4)–Sm(1)–Cn(2)	108.6	Cl(3)–Sm(2)–Cn(3)	104.8
Cl(3)–Sm(2)–Cl(3)′	81.5 (2)	Cn(3)–Sm(2)–Cn(3)′	127.8
Cl(3)′–Sm(2)–Cn(3)	114.3		

[a] Cn = centroid of ring.

Table VI. Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$

Distances			
Sm(1)–Cl(1)	2.76 (1)	Sm(1)–Cl(3)	2.623 (9)
Sm(2)–Cl(1)	2.764 (9)	Sm(2)–Cl(4)	2.65 (1)
Sm(3)–Cl(2)	2.77 (1)	Sm(4)–Cl(2)	2.89 (1)
Sm(4)–Cl(5)	2.60 (1)	Sm(1)–Cn(1)	2.45
Sm(1)–Cn(2)	2.43	Sm(2)–Cn(3)	2.45
Sm(2)–Cn(4)	2.45	Sm(3)–Cn(5)	2.44
Sm(3)–Cn(6)	2.46	Sm(4)–Cn(7)	2.41
Sm(4)–Cn(8)	2.47	Sm(5)–Cn(9)	2.48
Sm(5)–Cn(10)	2.48	Sm(3)–O(124)	2.56 (3)
Sm(5)–O(112)	2.56 (3)	Sm(5)–O(115)	2.46 (2)
Sm(5)–O(118)	2.72 (2)	O(112)–C(111)	1.45 (5)
O(112)–C(113)	1.27 (5)	O(115)–C(114)	1.48 (6)
O(115)–C(116)	1.49 (5)	O(118)–C(117)	1.52 (5)
O(118)–C(119)	1.44 (5)	O(121)–C(120)	1.49 (5)
O(121)–C(122)	1.43 (4)	O(124)–C(123)	1.47 (4)
O(124)–C(125)	1.48 (5)	C(113)–C(114)	1.68 (8)
C(116)–C(117)	1.47 (6)	C(119)–C(120)	1.61 (6)
C(122)–C(123)	1.57 (5)		
Angles			
Cl(1)–Sm(1)–Cl(3)	96.5 (3)	Cl(1)–Sm(1)–Cn(1)	104
Cl(1)–Sm(1)–Cn(2)	106	Cl(3)–Sm(1)–Cn(1)	104
Cl(3)–Sm(1)–Cn(2)	106	Cn(1)–Sm(1)–Cn(2)	133
Cl(1)–Sm(2)–Cl(4)	92.6 (3)	Cl(1)–Sm(2)–Cn(3)	108
Cl(1)–Sm(2)–Cn(4)	104	Cl(4)–Sm(2)–Cn(3)	103
Cl(4)–Sm(2)–Cn(4)	105	Cn(3)–Sm(2)–Cn(4)	135
Cl(2)–Sm(3)–O(124)	90.9 (7)	Cl(2)–Sm(3)–Cn(5)	105
Cl(2)–Sm(3)–Cn(6)	108	Cn(5)–Sm(3)–O(124)	103
Cn(6)–Sm(3)–O(124)	104	Cn(5)–Sm(3)–Cn(6)	136
Cl(2)–Sm(4)–Cl(5)	93.1 (3)	Cl(2)–Sm(4)–Cn(7)	106
Cl(2)–Sm(4)–Cn(8)	106	Cl(5)–Sm(4)–Cn(7)	106
Cl(5)–Sm(4)–Cn(8)	106	Cn(7)–Sm(4)–Cn(8)	133
Cn(9)–Sm(5)–Cn(10)	134	Cn(9)–Sm(5)–O(112)	102
Cn(9)–Sm(5)–O(115)	113	Cn(9)–Sm(5)–O(118)	102
Cn(10)–Sm(5)–O(112)	98	Cn(10)–Sm(5)–O(115)	113
Cn(10)–Sm(5)–O(118)	100	O(112)–Sm(5)–O(115)	62.1 (8)
O(112)–Sm(5)–O(118)	124.6 (8)	O(115)–Sm(5)–O(118)	62.6 (8)
Sm(1)–Cl(1)–Sm(2)	165.1 (4)	Sm(3)–Cl(2)–Sm(4)	164.8 (4)
Sm(5)–O(112)–C(111)	128 (3)	Sm(5)–O(112)–C(113)	121 (3)
C(111)–O(112)–C(113)	110 (4)	Sm(5)–O(115)–C(114)	131 (3)
Sm(5)–O(115)–C(116)	125 (2)	C(114)–O(115)–C(116)	100 (3)
Sm(5)–O(118)–C(117)	109 (2)	Sm(5)–C(118)–C(119)	123 (2)
C(117)–O(118)–C(119)	111 (4)	C(120)–O(121)–C(122)	104 (3)
Sm(3)–O(124)–C(123)	117 (2)	Sm(3)–O(124)–C(125)	122 (3)
C(123)–O(124)–C(125)	119 (3)	O(112)–C(113)–C(114)	119 (5)
C(113)–C(114)–O(115)	97 (3)	O(115)–C(116)–C(117)	103 (3)
C(116)–C(117)–O(118)	107 (4)	O(118)–C(119)–C(120)	105 (4)
C(119)–C(120)–O(121)	97 (3)	O(121)–C(122)–C(123)	105 (3)
C(122)–C(123)–O(124)	110 (4)		

Table VII. Comparison of Structural Data on $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ and $[(C_5Me_5)_2U(\mu\text{-}Cl)]_3$

M	Sm	U
M–Cl, avg, Å	2.876 (9)	2.901 (5)
M–C(ring), avg, Å	2.73 (4)	2.76 (3)
M–M, avg, Å	5.633 (2)	5.669 (2)
M radius,[46] avg, Å	0.964	1.025
Cl–M–Cl, avg, deg	83.2 (3)	84.5 (3)
M–Cl–M, avg, deg	156.7 (5)	155.5 (4)

$Me_2C_5H_3)_2Y(\mu\text{-}H]_3$[19] and the $[(C_5H_5)_2Ln(\mu\text{-}X)]_3(\mu_3\text{-}H)^-$ complexes (X = Cl, H) listed in Table I.[35] The latter two structures are significantly different in that they contain a central μ_3-hydride ligand.

$(C_5Me_5)_2ClSm(\mu\text{-}Cl)Sm(C_5Me_5)_2[\mu,\eta^4\text{-}Me(OCH_2CH_2)_4Me]\text{-}Sm(C_5Me_5)_2\}^+\{[(C_5Me_5)_2ClSm]_2(\mu\text{-}Cl)\}^-$ (**2**) also provides examples of new structural features for bis(pentamethylcyclopentadienyl)lanthanide complexes. These include an anionic single-halide-bridged bimetallic unit and a cationic $(C_5Me_5)_2Ln^+$ group. The most closely related structure in the literature for comparison with **2** is that of the yttrium complex $(C_5Me_5)_2ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$ (**3**).[14] Complexes **1**–**3** provide a variety of data which allow a detailed evaluation of structure and bonding in $[(C_5Me_5)_2LnZ]_n$ systems in general.

Trimers vs. Dimers. The first point for discussion is why $(C_5Me_5)_2SmCl$ adopts a trimeric as opposed to dimeric structure in the absence of coordinating solvents. Obviously, electrostatic and steric factors, two of the most important structural influences in organolanthanide chemistry,[2] must be considered. Electrostatic factors favor maximizing the number of anionic ligands around the charged samarium center. On the other hand, the size of the C_5Me_5 rings will limit the number of ligands which can interact for steric reasons. Both the trimeric structure and a dimeric structure with a planar doubly bridged $Sm_2(\mu\text{-}Cl)_2$ unit would provide a coordination number of eight for each samarium atom. A singly bridged dimeric structure analogous to that of $(C_5Me_5)_2ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$ must also be sterically accessible

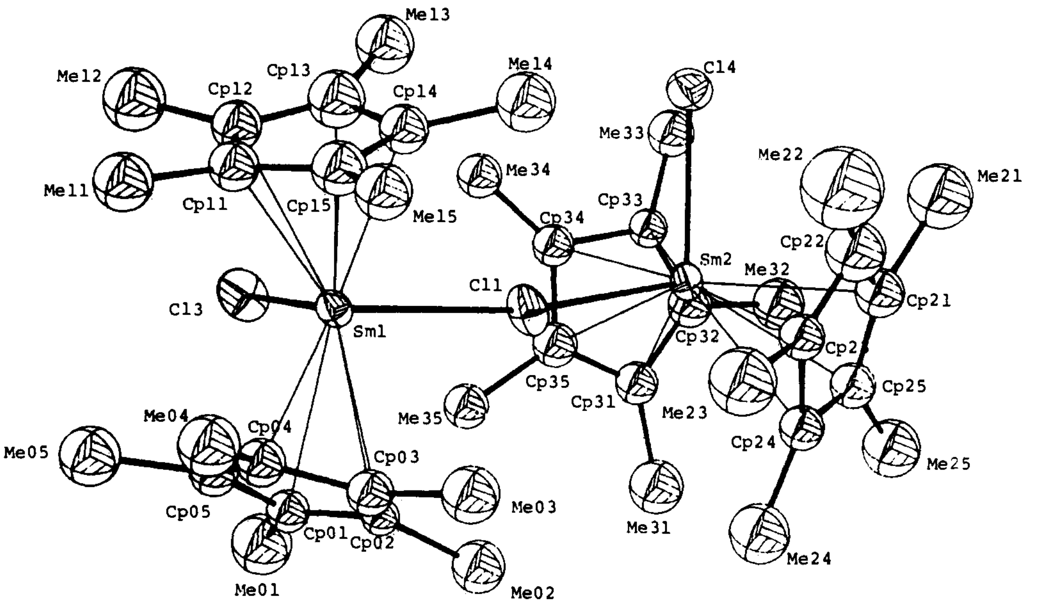

Figure 4. Structure of the $[(C_5Me_5)_2ClSm]_2(\mu\text{-}Cl)^-$ anion.

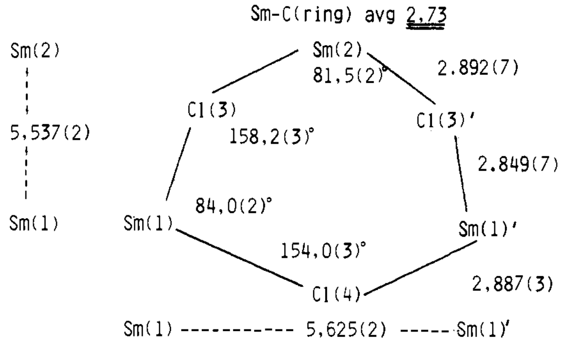

Figure 5. Selected bond lengths (Å) and angles (deg) in $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ (**1**).

to $(C_5Me_5)_2SmCl$ but would provide a coordination number of only seven for one of the samarium atoms. Electrostatic factors clearly favor the eight coordinate options.

It is possible that steric factors favor the observed trimeric structure over a dimeric alternative. The Sm···Sm nonbonding distances are particularly interesting in this regard (Figures 5 and 6). The Sm···Sm distances in the trimer, 5.625 (2) and 5.637 (2) Å, are longer than those in the singly bridged dimers in complex **2**, 5.61 (1) and 5.23 (1) Å, and are much longer than the Sm···Sm distance of 3.905 (3) Å in dimeric $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (**4**).[9] A dimeric $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_2$ complex would be expected to have a longer Sm···Sm distance than in **4**, but it would not be expected to exceed 5 Å with typical Sm–Cl–Sm bond distances and angles.[44] Hence, the trimeric structure allows the $(C_5Me_5)_2Sm$ units to be farthest apart while maintaining eight coordination for each metal.[45]

This analysis may be too simplistic, however. The existence of the five different coordination environments which we have found in this $(C_5Me_5)_2SmCl$ system indicates that there is no great preference for one type of geometry. Small, subtle changes in intra- and intermolecular steric interactions may cause a trimeric rather than a dimeric (or tetrameric) structure to form. Examination of intramolecular methyl–methyl contacts in **1**–**3** as well as in $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ shows that all of these structures have some methyl–methyl contacts less than the idealized 4.0-Å sum of van der Waals radii[46] both within and between $(C_5Me_5)_2Sm$ units. A proper analysis of the steric factors leading to trimer

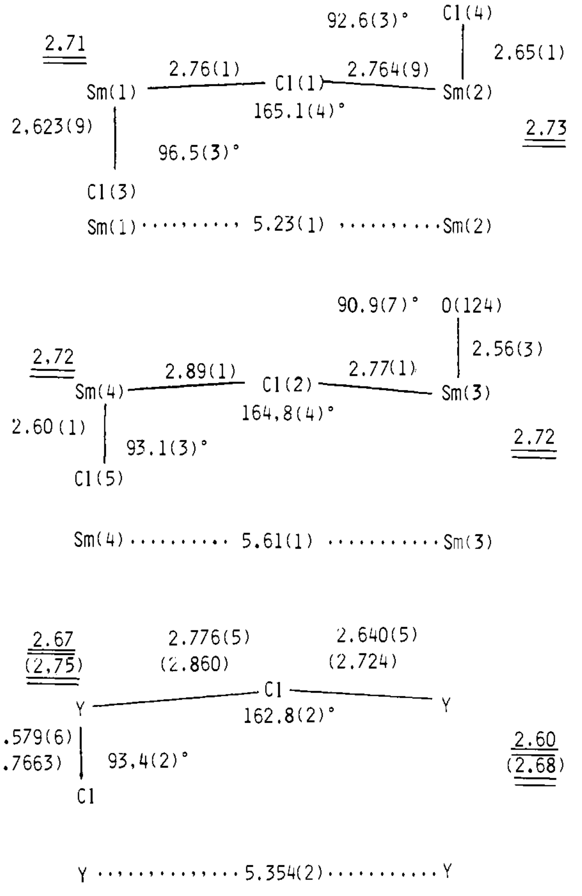

Figure 6. Selected bond lengths (Å) and angles (deg) in **2** and $(C_5Me_5)_2ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$. Double underlined numbers give average Ln–C(ring) distances. In the yttrium structure, the numbers in parentheses are enlarged by 0.084 Å to make them directly comparable to the samarium data. In the actual structures, the Sm(2)–Cl(4) and Sm(3)–O(124) vectors do not lie in the plane of the figure but are nearly perpendicular to the page.

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(44) For example, $\{[(Me_3Si)_2C_5H_3]_2Pr(\mu\text{-}Cl)\}_2$[17] has an average Pr–Cl distance of 2.81 Å, an average Pr–Cl–Pr angle of 101°, and a Pr···Pr distance of 4.338 Å. Assuming a 2.76-Å Sm–(μ-Cl) length and a 101° Sm–Cl–Sm angle, the Sm···Sm distance in "$[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_2$" would be 4.3 Å. An alternative comparison extrapolating from the Sm···Sm distance in $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ predicts a 4.7-Å Sm···Sm distance.

(45) $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)]_3$ is another neutral trimer which has long Ln···Ln distances compared to sterically similar dimeric systems of the same coordination number.

(46) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

formation would require a detailed summation of all of these contacts in the trimer as well as in the hypothetical $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_2$.

Note that halide-bridged organolanthanide dimers involving C_5Me_5 can be obtained if the steric congestion is reduced. $[(C_5Me_5)(THF)_2Sm(\mu\text{-}I)]_2$[47] is an example which has reduced steric crowding around the metal center since only one C_5Me_5 ligand is present and since the metal halide distances are longer for Sm^{2+}–I than for Sm^{3+}–Cl.

Another question relating to the structure of **1** is why $(C_5Me_5)_2ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$ does *not* exist as a trimer. As shown by the Sm···Sm distances in **1** and **2**, single-halide-bridged bimetallic structures can have the $(C_5Me_5)_2Ln$ units separated as far apart as in the trimeric structures. The 5.354 (2)-Å Y···Y distance in **3** is actually longer than the Sm(1)–Sm(2) distance of 5.23 (1) Å in **2** even though the radial size of Y^{3+} is 0.084 Å smaller than that of Sm^{3+}.[48] A trimeric structure for $(C_5Me_5)_2YCl$ would be more sterically crowded than that observed in **3** because all yttrium atoms would be eight coordinate. It is likely that **3** avoids the trimeric arrangement for that reason.

Metal Halide Distances. The structures of **1** and **2** contain several types of lanthanide chloride bridges and allow detailed structural comparisons to be made. The Sm–(μ-Cl) distances in trimeric **1**, 2.849 (7)–2.892 (7) Å, are on the long end of the range of values seen in **2**, 2.76 (1)–2.89 (1) Å. The distances in **1** are similar to those in $[(C_5Me_5)_2U(\mu\text{-}Cl)]_3$,[43] Table VII. The cyclic nature of the trimeric systems probably requires these longer M–(μ-Cl) distances. The cyclic nature of **1** also is probably responsible for the smaller 81–84° Cl–Sm–Cl angles in **1** vs. those of **2**, 91–96°, and the smaller 154–158° Sm–Cl–Sm angles vs. 164–166° in **2**. The uranium trimer has analogous angles which are similar to those in **1**.[43]

The two Sm–(μ-Cl) distances in the cationic component of **2**, $(C_5Me_5)_2ClSm(\mu\text{-}Cl)Sm(C_5Me_5)_2(\mu\text{-tetraglyme})Sm(C_5Me_5)_2^+$, are not equal (see Figure 6). The $(C_5Me_5)_2ClSm$–(μ-Cl) bridge bond is 0.12 Å longer than the (μ-Cl)–$Sm(C_5Me_5)_2(\mu\text{-tetraglyme})Sm(C_5Me_5)_2$ bridge. A similar situation is found in $(C_5Me_5)_2ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$: the $(C_5Me_5)_2ClY$–(μ-Cl) distance is 0.14 Å longer than the (μ-Cl)–$Y(C_5Me_5)_2$ distance. In the yttrium case, the difference in bridge distances could be explained in part by the difference in coordination number of the two metals. In **2**, however, both samarium atoms are eight coordinate. This suggests that electronic factors are important in governing these bond lengths. In each of the above cases, the longer bridge bond is associated with the $(C_5Me_5)_2Sm$ unit which has an additional terminal chloride ligand. This asymmetry is consistent with the lengthening of a Ln–Z bond expected as electron density from another ligand is added to the metal center. In this sense, these asymmetric halide structures give us a picture of a model intermediate in a reaction in which one bond is being broken at the metal center as it is attacked by an incoming nucleophile.

Consistent with the above analysis is the fact that the bridge in the anion $(C_5Me_5)_2ClSm(\mu\text{-}Cl)SmCl(C_5Me_5)_2^-$ in **2** *is* symmetrical. The bridge bonds in the anion are the shortest such distances in **2**. These distances are more similar to the (μ-Cl)–$Sm(C_5Me_5)_2(\mu\text{-tetraglyme})Sm(C_5Me_5)_2^+$ distance and the (μ-Cl)–$(C_5Me_5)_2Y$ distance in **3** rather than to the $(C_5Me_5)_2ClLn$–(μ-Cl) distances in **2** and **3**. The relatively short $(C_5Me_5)_2ClSm$–(μ-Cl) distance in the anion must arise due to the full negative charge on that species. A $(C_5Me_5)_2ClLn$ unit will be attracted closer to a bridging halide atom with a formal negative charge than to a bridging halide which is part of a neutral $(C_5Me_5)_2LnCl$ unit.

The terminal Cl–Sm distances in **2** are shorter than the bridging (μ-Cl)–Sm distances in **1** and **2**, as is commonly observed for a range of ligands in organolanthanide chemistry.[5,28,47] The 2.60 (1) Å Sm(4)–Cl(5) distance in the neutral part of the cation is shorter than the 2.623 (9) and 2.65 (1) Å Sm–Cl distances in the anion. This is reasonable considering that the $(C_5Me_5)_2ClSm$ unit in the cation is further from its bridging chloride ligand, 2.89 (1) Å, than the $(C_5Me_5)_2ClSm$ units in the anion are from their bridging chloride ligands, 2.76 (1) and 2.764 (9) Å. A longer Sm–(μ-Cl) distance is associated with a shorter Sm–Cl terminal bond length. All of the terminal Sm–Cl distances in **2** are shorter than the terminal Sm–Cl distances of 2.709 (8) and 2.765 (8) Å found in the structure of neutral, monomeric $(C_5Me_5)_2SmCl(THF)$.[28] All of these distances fall within the range of terminal Ln–Cl distances found in a recent compilation of organolanthanide halide structural data.[14]

Other Structural Features. The average Sm–C(C_5Me_5 ring) distances are essentially unaffected by the presence of the $(C_5Me_5)_2Sm$ unit in a neutral, cationic, or anionic complex or in a dimeric or cyclic trimeric environment. These distances for the two crystallographically independent eight-coordinate Sm centers in the trimer **1**, and the four types of eight-coordinate Sm in **2**, all fall in the range 2.70–2.74 Å. The C_5Me_5 rings attached to the formally nine-coordinate Sm(5) in the tetraglyme-solvated chloride-free part of the cation in **2** have similar average Sm–C(C_5Me_5 ring) distances of 2.73 and 2.76 Å (see below). These data can be compared to average Sm–C(C_5Me_5 ring) distances in other $(C_5Me_5)_2Sm(X)(Y)$ systems which range from as small as 2.68 Å in seven-coordinate $(C_5Me_5)_2Sm(OC_6Me_4H)$[50] to 2.77 Å in $[(C_5Me_5)_2(Ph_3PO)Sm]_2(\mu\text{-}OCH{=}CHO)$.[51]

The Sm(3)–O(124) distance of 2.56 (3) Å and the Sm(5)–O(115) and Sm(5)–O(112) distances of 2.46 (2) and 2.56 (3) Å are close to the range of observed Sm(III)–O(ether) donor interactions observed in other $(C_5Me_5)_2Sm$ systems.[52] However, the Sm(5)–O(118) distance of 2.72 (2) is quite long. The orientation of the tetraglyme chain of atoms is such that O(118) is directed toward Sm(5) indicative of a donor O → Sm interaction. The long distance suggests that the interaction is not as strong as those involving oxygens O(12) and O(15) and hence Sm(5) may not be a fully nine-coordinate Sm center. This would explain the similarity of the average Sm(5)–C(C_5Me_5 ring) distance to the average for the other samarium atoms.[13]

Conclusion

The X-ray crystal studies of complexes **1** and **2** provide important data regarding structural trends for bis(pentamethylcyclopentadienyl)lanthanide complexes. Together these complexes clearly show the variation in coordination geometry which is possible for a single set of ligands. The four different samarium coordination environments in **2** constitute the most remarkable example of this. Lanthanide complexes traditionally have been thought to be flexible in their coordination geometries since geometry-specific orbital effects are not as important as in transition-metal chemistry. However, previous structural data have generally involved the isolation of a single preferred structural type for a given metal and ligand set. The $(C_5Me_5)_2SmCl$ system is clearly more versatile. Other combinations of ligands and lanthanide metals which have the same steric balance between the metal and ligands as is found in $(C_5Me_5)_2SmCl$ can also be expected to have a variety of coordination environments available.

It is possible that the steric balance in $(C_5Me_5)_2SmCl$ is special in this regard. For example, it may be that the size of two C_5Me_5 rings and a chloride ligand relative to Y^{3+} allows only one type of preferred geometry. In contrast, with the larger Sm^{3+} ion, the balance of ligand vs. metal size may allow more flexibility in stable coordination geometries. Note that yttrium with the smaller cyclopentadienyl ring, 1,3-$Me_2C_5H_3$, has more demonstrated structural flexibility.[19] For example, (1,3-$Me_2C_5H_3)_2YH$ units crystallize in an eight-coordinate unsolvated trimeric state *and*

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in a nine-coordinate solvated dimeric form (Table I).

Too little data are available to generalize further. However, as more structural information is gathered and the quantitative analysis of steric factors in organolanthanide chemistry becomes more refined,[53,54] it may be possible to predict which ligand–metal combinations will be flexible and which will not. This could be quite useful in controlling reactivity.[2]

Another conclusion obtainable from this study is the importance of the steric bulk of $(C_5Me_5)_2Ln$ units in polymetallic organolanthanide complexes. The preferred tetrahedral disposition of C_5Me_5 ring centroids in **2**, which clearly has a variety of available geometries, reemphasizes the preference for this arrangement already found in $[(C_5Me_5)_2Sm]_2(\mu\text{-O})$,[55] $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$, and $(C_5Me_5)_2ClY(\mu\text{-Cl})Y(C_5Me_5)_2$. If a $(C_5Me_5)_2Ln$ unit cannot satisfy its coordination needs *and* have a tetrahedral ring centroid arrangement in a bimetallic complex, it will adopt a more highly oligomerized form which has a greater distance between $(C_5Me_5)_2Ln$ units. Hence unsolvated $(C_5Me_5)_2SmCl$ trimerizes. Given the importance of bridging vs. nonbridging ligands to reactivity,[2] knowledge of the tendency of a system to oligomerize is essential to understanding reactivity patterns.

Finally, the structural data on **1** and **2** emphasize further the remarkable nature of $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$. The small size of the hydride ligands allows this $(C_5Me_5)_2SmZ$ system to achieve eight coordination in a dimeric structure with a tetrahedral arrangement of the C_5Me_5 rings. This may not be possible with ligands other than hydride.

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Supplementary Material Available: Completely numbered plot of the cation in **2** and tables of bond distances, angles, and thermal parameters (7 pages); tables of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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Formation of Imidates, Amides, Amines, Carbamates, and Ureas from the μ_3-NPh Ligands of $Fe_3(\mu_3\text{-NPh})_2(CO)_9$

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Abstract: The bis(nitrene) cluster $Fe_3(\mu_3\text{-NPh})_2(CO)_9$ (**1**) reacts with $Li[HBEt_3]$, MeLi, PhLi, and NaOMe to form the formyl and acyl clusters $[Fe_3(\mu_3\text{-NPh})_2(CO)_8C\{O\}R]^-$ (**4**, R = H; **6**, R = Ph; **7**, R = Me; **8**, R = OMe). Formyl cluster **4** is unstable at room temperature and slowly loses CO to form the hydride cluster $[HFe_3(\mu_3\text{-NPh})_2(CO)_8]^-$. The benzoyl cluster **7** reacts with EtOTf to yield the nitrene–carbene cluster $Fe_3(\mu_3\text{-NPh})_2(CO)_8(C\{OEt\}Ph)$ (**9**) which has been structurally characterized: *Pbca*, $a = 13.668$ (6) Å, $b = 17.588$ (7) Å, $c = 25.644$ (8) Å, $V = 6164$ (7) Å^3, $Z = 8$, $R = 0.060$, $R_w = 0.075$ for 2982 reflections with $F_o > 2\sigma(F_o)$. The carbene ligand is bound to a basal iron atom, and the carbene carbon lies within the Fe_3 plane. The carbene and nitrene ligands in **9** couple to form the imidate PhN=C(OEt)Ph when **9** is exposed to air or allowed to stand in solution for prolonged periods under CO or N_2 atmospheres. A crossover experiment showed this coupling to be strictly intramolecular. Similar nitrene–benzoyl coupling from **7** gives benzanilide, and the methoxycarbonyl and nitrene ligands in **8** couple to give methyl *N*-phenylcarbamate when the clusters are oxidatively degraded with $[FeCp_2]^+$. The latter reaction models mechanistic suggestions previously made for the $M_3(CO)_{12}$ (M = Fe, Ru) catalyzed carbonylation of $PhNO_2$ to yield carbamates. The bis(phosphinidene) cluster $Fe_3(\mu_3\text{-PPh})_2(CO)_9$ (**2**) also reacts with PhLi to yield a benzoyl derivative, $[Fe_3(\mu_3\text{-PPh})_2(CO)_8(C\{O\}Ph)]^-$. However, addition of EtOTf to this species does not result in a carbene cluster analogous to **9**, but instead phosphinidene–carbene coupling occurs to give $Fe_3(\mu_3\text{-PPh})(\mu_3\text{-PhPC}\{OEt\}Ph)(CO)_9$ which has been structurally characterized: $P\bar{1}$, $a = 9.241$ (2) Å, $b = 10.233$ (3) Å, $c = 19.564$ (5) Å, $\alpha = 84.53$ (2)°, $\beta = 84.43$ (2)°, $\gamma = 76.41$ (2)°, $V = 1784.7$ (8) Å^3, $Z = 2$, $R = 0.0557$, $R_w = 0.0602$ for 3710 reflections with $F_o > 3\sigma(F_o)$. The phosphorus atom of the μ_3-PhPC{OEt}Ph ligand bridges two iron atoms, and the ethoxy-substituted carbon is attached to the third iron atom.

The chemistry of low-valent metal carbene complexes has been extensively investigated, and many such compounds have found impressive synthetic utility.[1] In contrast, the chemistry of *nitrene* ligands bound to low-valent metals remains relatively unexplored,[2] even though such ligands have been invoked as intermediates in several catalytic reactions.[3] The lack of chemical studies is in part due to the low stability of *mononuclear* carbonyl nitrene complexes such as $(CO)_5Cr{=}NPh$,[4] a particularly interesting species in view of the large number of synthetic applications of its carbene analogue.[1c] Like many reactive organic ligands, stabilization of nitrenes by low-valent organometallics can be

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