Journal of Organometallic Chemistry, 433 (1992) 79–94
Elsevier Sequoia S.A., Lausanne
JOM 22600

Structural trends in bis(pentamethylcyclopentadienyl)lanthanide and yttrium complexes

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(Received October 2, 1991)

Abstract

Structural data on over 90 bis(pentamethylcyclopentadienyl) lanthanide and yttrium complexes are presented and analyzed to define trends in structural parameters. Comparative data useful in evaluating structural aspects of molecules to be crystallographically characterized in the future are presented.

Introduction

In recent years there has been a rapid expansion in the number of X-ray structural determinations performed on organolanthanide and organoyttrium complexes. There are several reasons why so many X-ray crystallographic studies have been done on this particular class of complexes. First, since many of the metals are paramagnetic [1], NMR characterization is often not definitive and cannot be used as commonly as it is in transition metal chemistry. Second, since steric factors are so important in determining the organometallic chemistry of these metals [2], structural data are often essential to understand observed reactivity patterns. Third, there are now numerous cases [3–14] in which the basic connectivity of the atoms in the molecule was known without a crystallographic determination, but the X-ray crystal study revealed an unexpected structural feature, *e.g.*, an unusual bond length, asymmetry, agostic interaction, *etc.*, which often was one of the most significant new aspects of the molecule! Without the X-ray study, these important features would have been missed.

So many new organolanthanide and organoyttrium structures have appeared in the literature since the last structural reviews of this area were published [15–18] that it is currently difficult to compare new structural data with published

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Table 1

Structural parameters in trivalent bis(pentamethylcyclopentadienyl) lanthanide and yttrium complexes

Formula ($Cp^* = C_5Me_5$)	Formal metal coordination number	Ln–C(Cp* ring) average distance (Å)	(Cp* ring centroid)–metal–(Cp* ring centroid) angle (deg)	Ln–C(non-Cp*) distance (Å)	Ln–O(THF) distance (Å)	Heteroatom, Ln–heteroatom distance (Å)	Reference
Lanthanum							
$[Cp^*_2La(\mu\text{-}\eta^1:\eta^1\text{-}CH_2CN)]_2$	8	2.81(1)	–	2.748(4)	–	N, 2.537(4)	76
$[Cp^*_2La(THF)(\mu\text{-}\eta^1:\eta^3\text{-}C_4H_6)\mathit{La}Cp^*_2]$	8	–	129.56(5)	2.734(4) 2.759(4) 2.688(4)	–	–	72
$[Cp^*_2\mathit{La}(THF)(\mu\text{-}\eta^1:\eta^3\text{-}C_4H_6)LaCp^*_2]$	8	–	134.25(5)	2.633(4)	2.637(3)	–	72
Cerium							
$Cp^*_2CeI(NCMe)_2$	9	2.80(2)	135	–	–	N, 2.63(2) I, 3.231(2)	40
$Cp^*_2Ce(\mu\text{-}Cl)_2Li(OEt_2)_2$	8	–	–	–	–	Cl, 2.812(1)	39
$[Cp^*_2Ce(\mu_3\text{-}Cl)_2K(THF)]_n$	8	2.79(2)	136	–	–	Cl, 2.777(1)	57
$Cp^*_2Ce[CH(SiMe_3)_2]$	7 [a]	2.79(4) 2.78(4)	–	2.535(5)	–	–	12
Praseodymium							
$Cp^*_2Pr(\mu\text{-}Cl)_2Na(DME)_2$	8	2.795(20) 2.77(2)	134.9(7) 135.5(7)	–	–	Cl, 2.728(5) 2.747(8)	68
Neodymium							
$Cp^*_2Nd[CH(SiMe_3)_2]$	7 [a]	2.76(3)	134.4	2.517(7)	–	–	14
Samarium							
$Cp^*_2\mathit{Sm}(\mu\text{-}\eta^4:\eta^2\text{-}CH_2CHPh)\text{-}SmCp^*_2$	10	2.792(36)	127.4	2.674(15) 2.732(15)	–	–	8
$Cp^*_2Sm(\eta^3\text{-}CH_2CHCHPh)(OC_8H_8)$	9	2.77(2)	134.6	2.78(11)	–	–	65
$Cp^*_2Sm(\eta^5\text{-}C_5H_5)$	9	2.770(3)	127.0	2.738(4)	–	–	56
$Cp^*_2\mathit{Sm}(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_5)SmCp^*_2$	9	2.766(3)	127.8	2.800(4)	–	–	56
$[Cp^*_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3$	9	2.75(2)	133.0 135.1	2.58(2) 2.57(2)	–	–	58

$Cp^*_2Sm(\eta^2\text{-}PhN_2Ph)(THF)$	9	2.76(2)	135.9 137.6	–	2.532(8) 2.577(9)	N, 2.39(1) 2.43(1) 2.40(1) 2.45(1)	60
$[Cp^*_2Sm(THF)]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2C_4H_4\text{-}C_4H_4N_2)$	9	2.752(8)	134.2	–	2.555(5)	N, 2.351(6) 2.430(6)	62
$Cp^*_2SmI(\eta^2\text{-tetrazole})$	9	2.73(2)	137	–	–	I, 3.100(2) N, 2.81(2) 2.54(1)	21
$[Cp^*_2ClSm(\mu\text{-}Cl)SmCp^*_2(\mu\text{-}\eta^1:\eta^3\text{-tetraglyme})\mathit{Sm}Cp^*_2]^+$	9	2.74(5)	134	–	–	O, 2.56(3) 2.46(2) 2.72(2)	55
$[Cp^*_2\mathit{Sm}(\mu\text{-}\eta^1:\eta^1:\eta^2\text{-}O_2CCCO)(THF)SmCp^*_2]_2$	9	2.73(3)	132.9	2.77(2)	–	O, 2.39(1) 2.38(1)	50
$Cp^*_2SmMe(THF)$	8	2.711(6)	139.4	2.484(14)	2.473(9)	–	61
$Cp^*_2Sm(CH_2Ph)(THF)$	8	2.755(2)	133.8	2.528(8)	2.498(5)	–	67
$Cp^*_2SmPh(THF)$	8	2.737(13)	136.9	2.511(8)	2.511(4)	–	46
$Cp^*_2\mathit{Sm}(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)SmCp^*$	8	2.744(21)	135.4	2.638(7)	–	H, 2.05(11)	67
$[Cp^*_2Sm(\mu\text{-}Me)_2AlMe_2]_2$	8	2.68(1)	138.5	2.75(2)	–	–	61
$Cp^*_2Sm(\mu\text{-}Et)_2AlEt_2$	8	2.712(2)	134.2	2.662(4)	–	–	5
$Cp^*_2Sm(C{\equiv}CPh)(THF)$	8	2.71(3)	136.9	2.50(2)	2.49(1)	–	66
$Cp^*_2Sm(\eta^3\text{-}CH_2CHCH_2)$	8	2.724(4)	140.3	2.647(16)	–	–	65
$Cp^*_2Sm(\eta^3\text{-}CH_2CHCHMe)$	8	2.73(2) 2.73(3)	138.9 139.1	2.65(7) 2.64(4)	–	–	65
$(Cp^*_2Sm)_2(\mu\text{-}\eta^3:\eta^3\text{-}CH_2CHCHCH_2CH_2CHCHCH_2)$	8	2.729(3)	138.3	2.66(6) 2.66(7)	–	–	65
$Cp^*_2Sm(\mu\text{-}\eta^4:\eta^2\text{-}CH_2CHPh)\mathit{Sm}Cp^*_2$	8	2.718(25)	135.9	2.537(15) 2.647(15)	–	–	8
$(Cp^*_2Sm)_2(\mu\text{-}\eta^2:\eta^2\text{-}PhCCCCPh)$	8	2.71(2)	133.9	2.48(1) 2.76(1)	–	–	20,54
$[Cp^*_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}{}^tBuCPPC{}^tBu)$	8	–	–	2.557(6) 2.556(6)	–	P, 2.952(2) 2.945(2)	41
$[Cp^*_2Sm(CNCMe_3)]_2(\mu\text{-}O)$	8	2.80(1)	133.5 131.9	2.62(1) 2.66(1)	–	O, 2.101(7) 2.117(7)	21
$[Cp^*_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$	8	2.73(2)	134.9 140.0	–	–	N, 2.347(6) 2.368(6)	7

Table 1 (continued)

Formula ($Cp^* = C_5Me_5$)	Formal metal coordination number	Ln–C(Cp* ring) average distance (Å)	(Cp* ring centroid)–metal–(Cp* ring centroid) angle (deg)	Ln–C(non-Cp*) distance (Å)	Ln–O(THF) distance (Å)	Heteroatom, Ln–heteroatom distance (Å)	Reference
$Cp^*_2Sm(bipy)$	8	2.724(3)	134.8	–	–	N, 2.427(2) 2.436(2)	62
$(Cp^*_2Sm)_2[\mu\text{-}\eta^2:\eta^2\text{-}(PhCH{=}NNCHPh)_2]$	8	2.76(2)	134.1 132.8	–	–	N, 2.315(13) 2.431(14) N, 2.350(12) 2.411(13)	62
$(Cp^*_2Sm)_2(\mu\text{-}\eta^2:\eta^2\text{-}pyCH{=}C(O)C(O){=}CHpy)$	8	2.71(1)	140.8	–	–	O, 2.191(6) N, 2.473(7)	59
$(Cp^*_2Sm)_2[(\mu\text{-}\eta^2:\eta^2\text{-}(OCNPh)_2]$	8	2.71(1)	138.3	–	–	O, 2.30(1) N, 2.49(1)	53
$[Cp^*_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1\text{-}O_2C_{16}H_{10})$	8	2.75(2)	132.9	–	2.490(9)	O, 2.099(9)	21
$[Cp^*_2Sm(\mu\text{-}\eta^1:\eta^1:\eta^2\text{-}O_2CCCO)\text{-}SmCp^*_2(THF)]_2$	8	2.70(3)	135.2	–	2.47(1)	O, 2.25(1)	50
$[Cp^*_2Sm(OPPh_3)]_2[\mu\text{-}\eta^1:\eta^1\text{-}cis\text{-}OCHCHO]$	8	2.770(25)	133.2 132.6	–	–	O, 2.147(10) 2.179(10) 2.392(10) 2.393(10)	49
$[Cp^*_2Sm(OPPh_3)]_2(\mu\text{-}\eta^1:\eta^1\text{-}trans\text{-}OCHCHO]$	8	2.77(3)	132.6 131.4	–	–	O, 2.122(8) 2.107(7) 2.355(7) 2.391(7)	49
$[Cp^*_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1\text{-}OSiMe_2OSiMe_2O)$	8	2.75(3)	135.5	–	2.465(5)	O, 2.157(5)	67
$Cp^*_2Sm[O(CH_2)_4C_5Me_5](THF)$	8	2.76(3)	135.1	–	2.49(1)	O, 2.08(1)	66
$[Cp^*_2Sm(\mu\text{-}OC)_2FeCp^*]_2$	8	2.694(9)	–	–	–	O, 2.348(4) 2.339(4)	42
$[Cp^*_2Sm(THF)_2]^+$	8	2.69(2)	134.2	–	2.46(1)	–	66
$Cp^*_2SmCl(THF)$	8	2.71(2)	133 (1) 136 (1)	–	2.48(2) 2.44(2)	Cl, 2.709(8) 2.765(8)	24

$[\mathrm{Cp}^*_2\mathrm{Cl}\mathit{Sm}(\mu\text{-Cl})\mathit{Sm}\mathrm{Cp}^*_2(\mu\text{-tetraglyme})\mathrm{SmCp}^*_2]^+$	8	2.72(3) 2.72(5)	136 133	–	–	(μ-Cl), 2.77(1) (μ-Cl), 2.89(1) O, 2.56(3) Cl, 2.60(1)	55
$[(\mathrm{Cp}^*_2\mathrm{SmCl})_2(\mu\text{-Cl})]^-$	8	2.71(5) 2.73(4)	128.2 127.8	–	–	Cl, 2.623(9) 2.65(1) (μ-Cl), 2.76(1) 2.764(9)	55
$[\mathrm{Cp}^*_2\mathrm{Sm}(\mu\text{-Cl})]_3$	8	2.73(4)	128.2 127.8	–	–	Cl, 2.849(7) 2.892(7) 2.887(3)	55
$\mathrm{Cp}^*_2\mathrm{SmI(THF)}$	8	2.725(1)	136 .137	–	2.45(1)	I, 3.043(2) 3.053(2)	24
$[\mathrm{Cp}^*_2\mathrm{Sm}(\mu\text{-H})]_2$	8	2.76(3)	130.5	–	–	–	43
$(\mathrm{Cp}^*_2\mathrm{Sm})_2(\mu\text{-}\eta^1:\eta^1\text{-PhN}_2\mathrm{Ph})$	7 [a]	2.74(3)	133 (1)	–	–	N, 2.40(1) 2.41(1)	4
$\mathrm{Cp}^*_2\mathrm{Sm}(\mu\text{-H})(\mu\text{-}\eta^1:\eta^5\text{-CH}_2\mathrm{C}_5\mathrm{Me}_4)\mathit{Sm}\mathrm{Cp}^*$	7	2.715(20)	131.0	–	–	H, 2.11(9)	67
$(\mathrm{Cp}^*_2\mathrm{Sm})_2(\mu\text{-O})$	7	2.73(1)	137.2	–	–	O, 2.094(1)	45
$\mathrm{Cp}^*_2\mathrm{Sm(OC}_6\mathrm{Me}_4\mathrm{H)}$	7	2.68(1)	139.1	–	–	O, 2.13(1)	51
$(\mathrm{Cp}^*_2\mathrm{Sm})_2(\mu\text{-}\eta^1:\eta^1\text{-O}_2\mathrm{C}_{16}\mathrm{H}_{10})$	7	2.70(3)	139.8	–	–	O, 2.08(2)	52
Yttrium							
$\mathrm{Cp}^*_2\mathrm{Y}[\eta^2\text{-C(CH}_2\text{-3,5-xylyl)=N(2,6-xylyl)}](\mathrm{THF}\text{-}d_8)$	9	2.728(5)	132.0(5)	2.392(3)	2.466(3)	N, 2.407(3)	13
$\mathrm{Cp}^*_2\mathrm{YMe(THF)}$	8	2.72(2) 2.61(6)	137.0(3)	2.44(2)	2.379(8)	–	75
$[\mathrm{Cp}^*_2\mathrm{Y}(\mu\text{-Me})_2\mathrm{AlMe}_2]_2$	8	–	–	2.65(2) 2.67(2)	–	–	78
$\mathrm{Cp}^*_2\mathrm{Y}(\mu\text{-C}{\equiv}\mathrm{CCMe}_3)_2\mathrm{Li(THF)}$	8	2.65(1)	138.3	2.38(2)	–	–	64
$\mathrm{Cp}^*_2\mathrm{YCl(THF)}$	8	2.650(14) 2.659(15)	136.2(4) 136.6(4)	–	2.410(7)	Cl, 2.579(3) 2.577(3)	24
$\mathrm{Cp}^*_2\mathrm{Y}(\mu\text{-Cl})\mathit{Y}\mathrm{ClCp}^*_2$	8	2.67(1)	135.8	–	–	Cl, 2.579(6) 2.776(5)	48
$\mathrm{Cp}^*_2\mathrm{Y[CH(SiMe}_3)_2]$	7 [a]	2.668(4)	134.4	2.468(7)	–	–	74

Table 1 (continued)

Formula ($Cp^* = C_5Me_5$)	Formal metal coordination number	Ln–C(Cp* ring) average distance (Å)	(Cp* ring centroid)–metal–(Cp* ring centroid) angle (deg)	Ln–C(non-Cp*) distance (Å)	Ln–O(THF) distance (Å)	Heteroatom, Ln–heteroatom distance (Å)	Reference
$Cp^*_2Y[N(SiMe_3)_2]$	7 [a]	2.667(4) 2.687(4) 2.666(4) 2.690(4)	132.4 132.2	–	–	N, 2.274(5) 2.253(5)	74
$Cp^*_2\mathit{Y}(\mu\text{-}Cl)YClCp^*_2$	7	2.60(2)	139 (3)	–	–	Cl, 2.640(5)	48
Holmium							
$Cp^*_2HoCl(THF)$	8	2.666(6)	135.6(2) 137.2(1)	–	2.382(3) 2.365(3)	Cl, 2.577(1) 2.578(1)	71
Ytterbium							
$[Cp^*_2\mathit{Yb}]_2[(\mu\text{-}C{\equiv}CPh)_4Yb]$	8	2.61(2)	–	2.40(2)	–	–	32
$Cp^*_2Yb(SPh)(NH_3)$	8	2.64(2)	136.2 136.9	–	–	N, 2.423(8) 2.432(8) S, 2.670(3) 2.679(3)	38
$Cp^*_2Yb(TePh)(NH_3)$	8	2.63(2)	136.9	–	–	N, 2.50(1) Te, 3.039(1)	34
$Cp^*_2YbCl(\eta^1\text{-}Me_2PCH_2PMe_2)$	8	2.63(1) 2.66(4)	134.9	–	–	Cl, 2.532(3) P, 2.941(3)	31
$[Cp^*_2Yb(\mu\text{-}OC)_2Mn(CO)_3]_2$	8	2.569(17) 2.579(14)	143.8	–	–	O (μ-CO), 2.268(4) 2.273(4)	30

$[Cp^*_2Yb(\mu\text{-}OC)_3Mn(CO)_2]_n$	8	2.59(2)	143.4	–	–	O (μ-CO), 2.401(5) 2.349(4) 2.417(5)	30
$[Cp^*_2Yb]_2[(\mu_3\text{-}OC)_4Fe_3(CO)_7]$	8	2.573(13)	141.6(6)	–	–	O (μ-CO), 2.243(4)	29
$Cp^*_2Yb(THF)(\mu\text{-}OC)Co(CO)_3$	8	2.596(2)	139.4(7)	–	2.335(2)	O (μ-CO), 2.258(2)	28
$\{Cp^*_2Yb\}_2\{(\mu_3\text{-}CO)_4Co_3[C_5H_4\text{-}(SiMe_3)]_2\}$	8	2.59(2)	140	–	–	O (μ-CO), 2.230(4)	37
$Cp^*_2Yb(\eta^2\text{-}S_2CNEt_2)$	8	2.63(3)	–	–	–	S, 2.70(1)	33
$(Cp^*_2Yb)_2(\mu\text{-}\eta^2:\eta^2\text{-}Te_2)$	8	2.626(16)	133.32	–	–	Te, 93.1513(9) 3.1598(7)	83
$Cp^*_2YbF(THF)$	8	2.628(5)	–	–	2.330(3)	F, 2.026(2)	79
$Cp^*_2YbF(OEt_2)$	8	2.631(4)	–	–	2.375(5)	F, 2.015(4)	79
$Cp^*_2YbCl(THF)$	8	2.64(1)	136.1(1)	–	2.37	Cl, 2.539(4)	81
$Cp^*_2Yb(\mu\text{-}Cl)_2AlCl_2$	8	2.58(2)	–	–	–	μ-Cl, 2.760(1) 2.752(1)	77
$Cp^*_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$	8	2.634(9)	–	–	–	μ-Cl, 2.593(1)	77
$Cp^*_2Yb(\mu\text{-}I)_2Li(OEt_2)_2$	8	2.625(4)	–	–	–	μ-I, 3.027(1)	77
$(Cp^*_2Yb)_2(\mu\text{-}Se)$	7	2.609(9)	138.94	–	–	μ-Se, 2.621(1)	35
$Cp^*_2Yb(\mu\text{-}F)YbCp^*_2$	7	2.58(2)	139	–	–	F, 2.084(2)	36
Lutetium complexes							
$Cp^*_2Lu(\mu\text{-}Me)_2PMe_2$	8	–	128.2(5)	2.344(15) 2.378(15)	–	–	69
$Cp^*_2Lu(\mu\text{-}SCMe_3)_2Li(THF)_2$	8	2.66(2)	131.5(3)	–	–	S, 2.709(3) 2.723(3)	70
$Cp^*_2LuCl(THF)$	8	2.63	137	–	–	Cl, 2.53	73

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[a] The actual coordination number may be higher due to interactions between the metal and parts of the ligand other than the donor atom.

Table 2

Structural parameters in divalent bis(pentamethylcyclopentadienyl) lanthanide complexes

Formula ($Cp^* = C_5Me_5$)	Formal metal coordination number	Ln–C(Cp* ring) average distance (Å)	(Cp* ring centroid)–metal–(Cp* ring centroid) angle (deg)	Ln–C(non-Cp*) distance (Å)	Ln–O(THF) distance (Å)	Heteroatom, Ln–heteroatom distance (Å)	Reference
Samarium							
$Cp^*_2Sm(THF)_2$	8	2.86(3)	136.8	–	2.64(2)	–	47
$Cp^*_2Sm(OC_5H_8)_2$	8	2.842(3)	138.2	–	–	O, 2.677(5)	63
$Cp^*_2Sm(DME)$	8	2.82(3)	140	–	–	O, 2.52(1) 2.61(2)	72
$Cp^*_2Sm(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_5)SmCp^*_2$	7	2.812(4)	139.7	2.986(8)	–	–	56
$Cp^*_2Sm(OC_5H_{10})$	7	2.816(3)	140.0	–	–	O, 2.630(6)	63
Cp^*_2Sm	6	2.79(1)	140.1	–	–	–	84
Europium							
Cp^*_2Eu	7	2.79(1)	140.3	–	–	–	84
Ytterbium							
$Cp^*_2Yb(NC_5H_5)_2$	8	2.74(4)	136.3(3)	–	–	N, 2.586(7) 2.544(6)	85
$Cp^*_2Yb(NH_3)(THF)$	8	2.78(4)	135.11	–	2.46(3)	N, 2.55(3)	80
$Cp^*_2Yb(\mu\text{-}Me)BeCp^*$	7[a]	2.680(3)	144.6	2.766(4)	–	–	11
$Cp^*_2Yb[(\mu\text{-}Et)AlEt_2(THF)]$	7	2.679(17)	142.8	2.854(18) 2.939(21)	–	–	82
$Cp^*_2Yb(\mu\text{-}C_1H_4)Pt(PPh_3)_2$	7[a]	2.67(2)	142.3	2.781(6)	–	–	10
$Cp^*_2Yb(MeC{\equiv}CMe)$	7	2.659(9)	143.3	2.850(10)	–	–	9
$Cp^*_2Yb(THF)$	7	2.672(14) 2.654(7)	143.5(3)	–	2.412(5)	–	27
$Cp^*_2Yb(\mu\text{-}F)YbCp^*_2$	7	2.69(2)	140	–	–	F, 2.317(2)	36

[a] The actual coordination number may be higher due to interactions between the metal and parts of the ligand other than the donor atom.

Table 3

Variation in range and average of metal–carbon (C_5Me_5 ring) distances as the metal changes for trivalent eight-coordinate $(C_5Me_5)_2$Ln complexes

	Metal radius (Å) [a]	Range of Ln–C(C_5Me_5) distances (Å)	Average of Ln–C(C_5Me_5) distances (Å)	Metal radius minus samarium radius (Å)	Average minus samarium average (Å)
La	1.16	2.81(1)	2.81(1)	0.081	0.08
Ce	1.143	2.79(2)	2.79(2)	0.064	0.06
Pr	1.126	2.77(2)–2.79(2)	2.78(1)	0.047	0.05
Sm	1.079	2.68(1)–2.80(1)	2.73(3)	0.0	0.0
Y	1.019	2.61(6)–2.72(2)	2.66(3)	−0.06	−0.07
Ho	1.015	2.666(6)	2.666(6)	−0.064	−0.06
Yb	0.985	2.57(2)–2.66(4)	2.61(3)	−0.094	−0.12
Lu	0.977	2.63–2.66(2)	2.645(15)	−0.102	−0.085

[a] Ref. 25.

Table 4

Variation in structural parameters as metal changes in $Cp_2^*LnCl(THF)$ complexes

Formula ($Cp^* = C_5Me_5$)	Metal radius (Å) [a]	Ln–C(ring) average distance (Å)	Ln–O(THF) distance (Å)	Ln–Cl distance (Å)	(Ring centroid)–metal–(ring centroid) angle (deg)	Reference
$Cp_2^*SmCl(THF)$	1.079	2.71(2)	2.48(2)	2.709(8)	133(1)	24
			2.44(2)	2.765(8)	136(1)	
$Cp_2^*YCl(THF)$	1.019	2.655(25)	2.410(7)	2.579(3)	136.2(4)	24
				2.577(3)	136.6(4)	
$Cp_2^*HoCl(THF)$	1.015	2.666(6)	2.382(3)	2.577(1)	135.6(2)	71
			2.365(3)	2.578(1)	137.2(1)	
$Cp_2^*YbCl(THF)$	0.985	2.64(1)	2.37	2.539(4)	136.1(1)	81
$Cp_2^*LuCl(THF)$	0.977	2.63	–	2.53	137	73
	Ln radius minus Sm radius (Å)		Ln–C average minus Sm–C average (Å)	Average Ln–O minus Sm–O (Å)	Average Ln–Cl minus Sm–Cl (Å)	
$Cp_2^*SmCl(THF)$	0		0	0	0	
$Cp_2^*YCl(THF)$	−0.06		−0.065	−0.05	−0.16	
$Cp_2^*HoCl(THF)$	−0.064		−0.054	−0.09	−0.16	
$Cp_2^*YbCl(THF)$	−0.094		−0.08	−0.09	−0.20	
$Cp_2^*LuCl(THF)$	−0.102		−0.09	–	−0.21	

[a] Ref. 25.

information. For example, the December 1980 compilation of structures in *Comprehensive Organometallic Chemistry* [19] listed only 21 yttrium and lanthanide structures and *only one* complex which contained the C_5Me_5 ligand. Indeed, it is possible that some new structural data are not evaluated to the fullest extent because a current compilation of relevant information is not available [20].

Accordingly, we have assembled structural data on complexes of this type in order to enumerate known structures in an organized way and to identify present trends in structural parameters. We have chosen to emphasize bis(pentamethylcyclopentadienyl) complexes of the lanthanides and yttrium since this is the most common class of crystallographically characterized complexes of these metals and readily provides a large data base with which to determine ranges of structural parameters.

Presentation of data

Table 1 presents the structural data on trivalent bis(pentamethylcyclopentadienyl) complexes. The data are first grouped according to metal in decreasing radial size. For each metal, complexes are arranged according to decreasing formal coordination number. Within the formal coordination number sub-categories, complexes with σ-bound carbon donor atom ligands are listed first. Complexes in which the third anionic ligand is a π-bound carbon ligand are listed next, followed by complexes with nitrogen, oxygen, and halide donor atoms. Ligands with donor atoms congeneric with C, N, and O are listed with the C, N, and O categories, respectively. Bimetallic complexes which contain metals with different coordination numbers are listed twice, once under each coordination number category.

Table 2 lists data for divalent complexes arranged in a similar order. For the purposes of this review, cyclopentadienyl and allyl ligands are considered to occupy three and two coordination positions, respectively (consistent with number of donor electron pairs). Non-classical metal ligand interactions such as agostic interactions are not included in the formal coordination number, but when such interactions are discussed in the original paper, this is indicated by a footnote.

Discussion of data

Several general features on structurally characterized lanthanide complexes are readily evident from Tables 1 and 2. The predominant coordination number found in these crystalline systems is eight. Hence, for metals the size of the lanthanides, a ligand set containing two C_5Me_5 groups and two additional electron pair donor ligands readily leads to crystallizable complexes. Despite this preference for eight-coordination, coordination numbers can range from six to ten in these systems.

Samarium is the metal which has the most crystallographic data in Table 1, although it is unlikely that this arises from any special propensity of the $(C_5Me_5)_2Sm$ unit to crystallize better than other $(C_5Me_5)_2Ln$ units. Instead, the high reactivity of Sm^{II}, which provides synthetic pathways not available to the other metals [2], and the paramagnetism of Sm^{II} and Sm^{III}, which limits NMR characterization compared with trivalent La, Y and Lu, are more likely reasons for the large number of crystallographically characterized samarium complexes.

Table 5

Variation in structural parameters as the metal changes in $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ complexes

Formula ($Cp^* = C_5Me_5$)	Ln radius (Å) [a]	Ln–C(ring) average distance (Å)	Ln–C(alkyl) (Å)	(Ring centroid)–metal–(ring centroid) angle (deg)	Reference
$Cp^*_2Ce[CH(SiMe_3)_2]$	1.143	2.79(4) 2.78(4)	2.535(5)	–	12
$Cp^*_2Nd[CH(SiMe_3)_2]$	1.109	2.76(3)	2.517(7)	134.4	14
$Cp^*_2Y[CH(SiMe_3)_2]$	1.019	2.668(4)	2.468(7)	134.4	74
	Ln radius minus Y radius (Å)	Ln–C(ring) average minus Y radius (Å)	Ln–C(alkyl) minus Y–C(alkyl) (Å)		
$Cp^*_2Ce[CH(SiMe_3)_2]$	0.124	0.012	0.07		
$Cp^*_2Nd[CH(SiMe_3)_2]$	0.090	0.09	0.05		
$Cp^*_2Y[CH(SiMe_3)_2]$	0	0	0		

[a] Ref. 25.

It is interesting to note, however, that currently available crystallographic data suggest that the $(C_5Me_5)_2Sm$ unit is the most flexible of the $(C_5Me_5)_2Ln$ moieties. No other single lanthanide has been found to exhibit the full, six to ten range of coordination numbers. In addition, samarium is the only metal which has provided pairs of closely related complexes of coordination number n and $n + 1$ both of which crystallize, *e.g.*, seven-coordinate $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1 : \eta^1\text{-}O_2C_{16}H_{10})$ and eight-coordinate $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1 : \eta^1\text{-}O_2C_{16}H_{10})$, seven-coordinate $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ and eight-coordinate $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$, and eight-coordinate $(C_5Me_5)_2SmI(THF)$ and nine-coordinate $(C_5Me_5)_2SmI(C_6H_{10}N_4)$ [21]. Generally, just one preferred coordination number would be expected to crystallize. For samarium, it is possible that the combination of its particular radial size with the steric bulk of two C_5Me_5 ligands may not have a single preferred coordination number compared with $(C_5Me_5)_2Ln$ units with lanthanides of other sizes. More structural data on other lanthanides are needed before this possibility can be fully established.

The data in Tables 1 and 2 are summarized and compared in Tables 3–6. In order to get the best comparisons, these tables focus on categories which are most common. Hence, Table 3 summarizes data on eight-coordinate complexes and shows how the average Ln–C(C_5Me_5 ring) distances decrease as the size of the metal decreases. The last two columns of Table 3, show the data normalized to the most common metal samarium. The similarity of the numbers in these two columns shows that the average distances parallel the metal radius as expected [15,16,22]. The entries for ytterbium in Table 3 are the least consistent with the trend, but this may be due to the particular set of eight-coordinate ytterbium complexes which have been crystallographically reported. The next comparison described below (Table 4) shows no anomaly for ytterbium. Obviously, when these tables are used to evaluate a newly characterized complex, the best comparisons will involve the

Table 6

Variation in structural parameters according to coordination number for $(C_5Me_5)_2Sm$ complexes

Coordination number	Metal radius (Å) [a]	Range of average Ln–C(Cp* ring) distances (Å)	Average of known Ln–C(Cp* ring) averages (Å)	Range of Ln–O(THF) distances (Å)	Average of Ln–O(THF) distances (Å)
Trivalent samarium complexes					
10 $Cp^*_2SmL_4$	–	2.79(4)	2.79(4)	–	–
9 $Cp^*_2SmL_3$	1.132	2.73(2)–2.77(2)	2.75(2)	2.53(1)–2.58(1)	2.56(2)
8 $Cp^*_2SmL_2$	1.079	2.68(1)–2.80(1)	2.73(3)	2.44(2)–2.511(4)	2.48(2)
7 Cp^*_2SmL	1.02	2.68(1)–2.74(3)	2.71(2)	–	–
Divalent samarium complexes					
8 $Cp^*_2SmL_2$	1.27	2.82(3) –2.86(3)	2.84(2)	2.64(2)	2.64(2)
7 Cp^*_2SmL	1.22	2.812(4)–2.816(3)	2.814(2)	–	–
6 Cp^*_2Sm	–	2.79(1)	2.79(1)	–	–

[a] Ref. 25.

specific metal with ligands with the most similar steric requirements [23] found in Tables 1 or 2.

Comparisons of bond length changes as the metal changes are continued in Tables 4 and 5. These tables use structural data for $(C_5Me_5)_2LnCl(THF)$ and $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$, which are the two most common specific classes of complexes in Table 1. In each case, the normalized data at the bottom of the table show that the Ln–C(ring) distances follow the trends expected on the basis of radial size. However, the Ln–O(THF), Ln–Cl, and Ln–C(alkyl) distances in Tables 4 and 5 do not follow the expected pattern as closely as the Ln–C(ring) distances. This type of variation has been observed previously in the metal halide distances [23,24].

Data on the effect of coordination number on Ln–C(C_5Me_5 ring) and Ln–O(THF) distances are summarized in Table 6 using samarium complexes. As expected, the distances increase with increasing coordination number and the increases are consistent with Shannon radii for metals with different coordination numbers [25].

A comparison of trivalent and divalent Ln–C distances is also presented in Table 6. For samarium complexes of the same coordination number, there is a clear distinction between the ranges of distances for trivalent and divalent species. For example, for eight-coordinate systems, the trivalent range is 2.68(1)–2.80(1) Å and the divalent range is 2.82(3)–2.86(3) Å. In fact, the trivalent and divalent distances nearly fall into two separate groups even if coordination number is not considered: for trivalent complexes in Table 6, the Sm–C average lengths do not exceed 2.80(1) Å and for divalent complexes, the Sm–C distances are 2.79(1) Å or larger. The overlap occurs between the rare examples of ten-coordinate Sm^{3+} and six-coordinate Sm^{2+}. As a result, Sm–C(C_5Me_5) distances for most samarium complexes are indicative of the valence state of the metal for a given coordination number. A similar situation obtains for ytterbium. Average Yb^{III}–C(C_5Me_5) distances range from 2.57(2)–2.66(4) Å whereas for Yb^{II} the range is 2.65(1)–2.78(4) Å.

Trivalent-divalent comparisons are also evident from pairs of entries in Tables 1 and 2 which differ *only* in oxidation state. For example, $[(C_5Me_5)_2Sm(THF)_2]^+$

and $(C_5Me_5)_2Sm(THF)_2$ have average Sm–C(C_5Me_5) distances of 2.69(2) and 2.86(3) Å, respectively. The Sm–O distances differ by a comparable amount, 2.46(1) and 2.64(2) Å. Similarly, the trivalent and divalent metal centers of $Cp^*_2Yb(\mu\text{-}F)YbCp^*_2$ exhibit Yb-C(C_5Me_5) distances of 2.58(2) and 2.69(2) Å, respectively. In this case, the Yb–F distances have a larger difference, 2.084(2) and 2.317(2) Å. These divalent-trivalent differences are in sharp contrast to differences in transition metal complexes of different valence [22]. For example, the average Fe–C distances found in $(C_5H_5)_2Fe^+$ ions, 2.067–2.076 Å, are actually larger than those in ferrocene, 2.045 Å [26].

Acknowledgments

We thank the National Science Foundation for support of this project and Dr. Joseph W. Ziller and Ms. Tammy LaFreniere for help in assembling the data.

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