Unprecedented Coordination of the AlH2+ and Na+ Cations in the Structure of the Organometallic Complex [AlH2(OC4H8)4][(.eta.5-C5H5)3Yb(.mu.-Na)Yb(.eta.5-C5H5)3]

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Organometallics, **1994**, 13 (5), 2075-2078• DOI: 10.1021/om00017a074 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Organometallics 1994, *13*, 2075–2078

Unprecedented Coordination of the AlH_2^+ and Na^+ Cations in the Structure of the Organometallic Complex $[AlH_2(OC_4H_8)_4][(\eta^5\text{-}C_5H_5)_3Yb(\mu\text{-}Na)Yb(\eta^5\text{-}C_5H_5)_3]$

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Received November 12, 1993[⊗]

Interaction of $Na[Yb(C_5H_5)_3]$ with aluminum hydride in THF yields the ionic complex $[AlH_2(C_4H_8O)_4][(C_5H_5)_3Yb(Na)Yb(C_5H_5)_3]$ (1) and $NaAlH_4$. This reaction apparently proceeds as an ionic exchange with the products of the autoionization of aluminum hydride in the solvent. Crystals of 1 are monoclinic, with $a = 8.494(2)$ Å, $b = 15.214(3)$ Å, $c = 18.242(4)$ Å, $\gamma = 92.45(2)°$, $Z = 2$, $\rho_{calcd} = 1.516$ g cm^{-3}, and space group $P2_1/b$. The structure was solved by the Patterson method and refined by full-matrix least-squares procedures to $R = 0.040$ and $R_w = 0.043$ for 2700 reflections with $I > 3\sigma(I)$. The metal atoms in 1 are bound by ionic bonds, forming a bent complex.

Introduction

The chemical behavior of Cp'_2Ln (Ln = Sm, Eu, Yb; $Cp' = C_5H_5$ or substituted cyclopentadienyl ligand) is determined by their Lewis acidity and high reduction potential.[1] Thus, these compounds are able to coordinate common Lewis n bases as well as weaker π-[2] and even σ-donor[3] ligands. However, the stability of the adducts noticeably depends on the nature of the metal. It is known that the interaction of samarocenes or the ate complex $Na[(C_5H_4{}^tBu)_3Sm]$ with AlR_3[4] and $AlH_3{\cdot}L$[5] proceeds as a redox reaction yielding the heterometallic alkyl or hydride complexes of samarium(3+) and aluminum via samarium(2+) adduct formation. The existence of this stage is confirmed by the isolation of the more stable (in comparison with the protium analog complex) $Cp''_2Sm(\mu\text{-}D)_2AlD{\cdot}Me_2NC_2H_4NMe_2$ ($Cp'' = C_5H_3{}^tBu_2$).[6] At the same time the ytterbium(2+) adducts $Cp^*_2YbMeBeCp$[3] and $Cp^*_2YbAlEt_3{\cdot}THF$[7] are rather stable and have been isolated.

On the basis of these facts, it might be expected that adducts of ytterbocenes with aluminum hydrides would be more stable with respect to redox reactions in comparison with the samarium analogs. Indeed, the reaction of $Na[Cp_3Yb]$ with aluminum hydride yields the unusual complex $[AlH_2(THF)_4][\eta^5\text{-}C_5H_5)_3Yb(\mu\text{-}Na)Yb(\eta^5\text{-}C_5H_5)_3]$ (1), whose structure is reported here.

Experimental Section

General Information. All manipulations were performed under dry argon or in vacuum using standard Schlenk techniques. All solvents were dried over $LiAlH_4$ and distilled before use under Ar. Chemicals were reagent grade. $YbI_2{\cdot}2THF$ was obtained by the literature method.[8] Ethereal solutions of aluminum hydride were prepared by the Schlesinger reaction from $LiAlH_4$ and $AlCl_3$.[9] Elemental analysis was performed with an AAS (Karl Zeiss, Jena) atomic absorption spectrometer and by the combustion method (C, H).

Synthesis of $Na[Yb(C_5H_5)_3]$. Powdered $YbI_2{\cdot}2THF$ (3.15 g, 6.0 mmol) was added in small portions to a freshly prepared solution of CpNa (18.0 mmol) in 150 mL of THF. The resulting dark-red solution was stirred 2 h and evaporated in vacuo to a thick consistency. Then, 150 mL of a benzene–THF mixture (3:1) was added. The white precipitate that formed was filtered off, and the filtrate was evaporated in vacuo. Subsequent vacuum-drying gave 1.76 g of $Na[Yb(C_5H_5)_3]$ as a yellow powder; yield 75%. The compound is easily oxidized and is soluble only in polar solvents (THF, DME). Anal. Calcd for $C_{15}H_{15}NaYb$: Yb, 44.24; Na, 5.88; C, 46.04; H, 3.86. Found: Yb, 44.3; Na, 6.0; C, 45.8; H, 3.9.

Synthesis of $[AlH_2(C_4H_8O)_4][(C_5H_5)_3Yb(Na)Yb(C_5H_5)_3]$ (1). $Na[Yb(C_5H_5)_3]$ (1.56 g, 4.0 mmol) was suspended in 150 mL of a benzene–THF mixture (3:1), and 35 mL of an ether solution of AlH_3 (4.0 mmol) and 0.6 mL of NEt_3 were added under stirring. The reaction mixture was stirred 2 h and was then filtered. Upon slow evaporation of the filtrate, green sticklike crystals of 1 formed. After decantation and vacuum-drying, 1.26 g of 1 (yield 60%) was obtained. Anal. Calcd for $C_{46}H_{64}O_4AlNaYb_2$: Yb, 34.18; Al, 2.66; Na, 2.27; C, 51.30; H, 5.99. Found: Yb, 34.2; Al, 2.4; Na, 2.4; C, 51.5; H, 6.1.

X-ray Data Collection and Reduction. X-ray-quality crystals of 1 were obtained by slow evaporation of the solution as described above. The single crystal was sealed in a glass capillary in vacuo and mounted on a Nicolet P3 diffractometer with Nb-filtered Mo Kα radiation for room-temperature data collection. The initial orientation matrices were obtained from 20 reflections located by au autosearch routine. These data were

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[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1994.

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0276-7333/94/2313-2075$04.50/0

Table 1. Crystallographic Data for Complex 1

compd	$[AlH_2(C_4H_8O)_4][(C_5H_5)_3Yb(Na)Yb(C_5H_5)_3]$
formula	$C_{46}H_{64}O_4AlNaYb_2$
fw	1076.56
color, habit	green, quadrangle sticks
cryst size, mm	0.5 × 0.3 × 0.3
cryst syst	monoclinic
space group	$P2_1/b$
a, Å	8.494(2)
b, Å	15.214(3)
c, Å	18.242(4)
γ, deg	92.45(2)
V, Å^3	2355.2(1.6)
Z	2
ρ_{calcd}, g cm^{-3}	1.516
radiation	Mo Kα
wavelength, Å	0.710 69
abs coeff, cm^{-1}	40.0
T, °C	22
scan type	$\theta/2\theta$
scan speed, deg min^{-1}	12
scan range, deg in ω	1.0 below K_1 to 1.0 above K_2
bkgd/scan time ratio	0.02
cryst decay	negligible
tot. no. of reflns	3210
index range	$h,+k,l$
2θ range, deg	3.5–50
no. of reflns with $I > 3\sigma(I)$	2700
no. of variables	245
R	0.040
R_w	0.043
largest e/Å^3 in final least-squares cycle	1.27[a]
GOF	1.26

[a] This peak is responsible for the Na atom statistic disorder.

Table 2. Atomic Coordinates (×10^4; hydrogen atom, × 10^3) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Complex 1

atom	x	y	z	B_{eq}
Yb	6984(1)	5126(1)	6592(1)	51(1)
Al	0	5000	0	69(2)
Na	4171(12)	5590(6)	5181(6)	106(3)
O1	−1044(10)	4076(5)	656(4)	90(3)
O2	−1407(10)	5899(1)	414(5)	90(3)
C1	7575(29)	6774(11)	6197(18)	154(11)
C2	8545(22)	6641(10)	6779(10)	111(8)
C3	9653(21)	6095(13)	6552(11)	130(9)
C4	9319(39)	5865(19)	5866(17)	212(16)
C5	8128(47)	6279(21)	5626(13)	210(18)
C6	7667(47)	3617(19)	7115(26)	275(24)
C7	8923(47)	3983(18)	7081(16)	255(18)
C8	9176(33)	3990(17)	6404(19)	190(16)
C9	8274(32)	3695(11)	5998(12)	125(9)
C10	6752(41)	3421(15)	6469(29)	319(29)
C11	5719(27)	5654(20)	7823(9)	257(15)
C12	5049(34)	6075(19)	7337(16)	204(16)
C13	4129(22)	5625(22)	7003(14)	161(12)
C14	4130(27)	4797(17)	7138(16)	193(12)
C15	5273(33)	4810(20)	7765(12)	232(14)
C16	−2279(29)	3501(18)	499(12)	232(15)
C17	−2506(27)	2895(12)	1047(11)	148(10)
C18	−1437(23)	3123(11)	1618(9)	119(8)
C19	−586(31)	3850(16)	1346(11)	211(13)
C20	−1139(21)	6470(14)	987(12)	177(11)
C21	−2386(23)	6979(11)	1134(11)	137(8)
C22	−3618(20)	6671(12)	618(11)	129(8)
C23	−2873(26)	6093(18)	166(14)	229(14)
H	114	530	57	80

Table 3. Main Interatomic Distances (Å) and Bond Angles (deg) for Complex 1

distances		angles	
Yb–CpI	2.372	CpI/CpII	119.5
Yb–CpII	2.364	CpI/CpIII	120.4
Yb–CpIII	2.391	CpII/CpIII	113.3
Yb–C	2.63(3)	Cp1YbCp2	117.6
Yb··Na	3.60(1)	Cp1YbCp3	115.7
Yb··Na′	3.54(1)	Cp2YbCp3	119.3
Na··Na′	2.42(2)	NaYbNa′	39.6(3)
Al–H	1.48()	YbNaYb	140.4(3)
Al–O1	2.021(8)	O1AlO2	89.5(2)
Al–O2	2.002(9)	HAlO1	93.4
		HAlO2	85.7

used to determine the crystal system. An automated check of the Laue symmetry confirmed the crystal system as monoclinic. Ultimately, 25 reflections (15° < 2θ < 35°) were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, crystal data, and data collection parameters are summarized in Table 1. The observed extinctions and subsequent refinements confirmed the space group as $P2_1/b$. The data sets were collected in four shells (3.5° < 2θ < 50°), and three standard reflections were recorded every 100 reflections. The intensities of the standards showed no statistically significant change over the duration of the data collection. The data were processed using the SHELXTL software program package on a Nova 3 workstation located at the L. Ya. Karpov Physico-Chemical Research Institute. The reflections with $I > 3\sigma(I)$ were used in the refinement.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[10] The heavy-atom positions were determined using the Patterson method employing the same program package. The remaining non-hydrogen atoms were located from successive Fourier map calculations. The refinements were carried out by using full-matrix, least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight, w, is defined as $1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of refinement, all the non-hydrogen atoms in 1 were refined as individual anisotropic atoms. The sodium atoms statistically occupy two positions with a weight of about $^1/_2$ around an inversion center at $1-x, 1-y, 1-z$. Positions of hydride hydrogen atoms were determined by difference Fourier synthesis. Positions of other hydrogen atoms bound to carbon atoms were calculated by assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.1 times the isotropic temperature factor of the carbon atom to which they are bonded. The final refinement data are given in Table 1. The following data are tabulated: positional parameters (Table 2) and selected bond distances and angles (Table 3). Thermal parameters (Table S1) and hydrogen atom parameters (Table S2) have been deposited as supplementary material.

Results and Discussion

The interaction of $Na[Cp_3Yb]$ with aluminum hydride in THF media is accompanied by a change of solution color from orange to yellow and the precipitation of green crystals in the form of quadrangle sticks. During the reaction we observed no H_2 evolution or aluminum metal precipitation; i.e., the reaction is not a redox reaction, unlike reaction 1,

$$Na[Cp_3Sm] + 2AlH_3{\cdot}THF \rightarrow {}^1/_2(Cp_2SmAlH_4{\cdot}THF)_2 + Al + H_2 + NaCp \quad (1)$$

describing the interaction of the analogous ate complex of samarium(2+) with $AlH_3{\cdot}THF$.[5] On the basis of elemental analysis, the compound obtained exhibits the ratio Na:Yb:Al = 1:2:1. X-ray analysis of the single crystal shows the composition described with formula 1, and consequently, its synthesis may be represented by eq 2.

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$$2Na[Cp_3Yb] + 2AlH_3{\cdot}THF \rightarrow [AlH_2(THF)_4][(Cp_3Yb)_2Na] + NaAlH_4 \quad (2)$$

According to the X-ray data, the crystals of **1** are built from discrete particles—the anion $[(\eta^5\text{-}C_5H_5)_3Yb\,(\mu\text{-}Na)Yb(\eta^5\text{-}C_5H_5)_3]^-$ (**1a**) and the cation $[AlH_2(THF)_4]^+$ (**1c**). In cation **1c**, the aluminum atom is located in a center of symmetry and has an octahedral environment with bond angles close to 90° (Figure 1a). Two hydride atoms occupy *trans* positions, and four THF molecules lie in an equatorial plane of the octahedron. An analogous cation has been detected in the ionic aluminum chloride tetrahydrofuranate $[AlCl_2(THF)_4]^+[AlCl_4]^-$.[11] However, the average Al–O distance of 1.94 Å in this complex is noticeably shorter than that found in **1** (Table 3) owing to the electron-withdrawing chloride ligands.

It should be noted that cationic hydride complexes of aluminum are extremely rare. Recently, only two related $[AlH_2L_n]^+$ complexes stabilized by penta- and tetraamines were documented.[12] In $[AlH_2(pmdien)]^+$ (pmedien = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine), the aluminum atom has a trigonal bipyramidal environment with *cis* positions for the hydrogen atoms, and in $[AlH_2(Me_4\text{-}cyclam)]^+$ (**2**) (Me_4cyclam = 1,4,8,11-tetramethyl-1,4,8,-11-tetraazatetradecane), Al has an octahedral environment with the hydrogens in *trans* positions, as in the case of **1**. In both cases, the crystal structures include the $[AlH_4]^-$ anions. The Al–H distance in **1c** is comparable with the distances in cation **2** (1.5 Å)[12] and in neutral and anionic complexes of aluminum hydride (1.5–1.8 Å).[13-15] The length of the Al–O-bond in **1c** is practically the same as those found in $[(C_5H_4{}^tBu)_2SmAlH_4{\cdot}THF]_2$ (2.00 Å)[6] and in $(Cp_2YAlH_4{\cdot}THF)_2$ (1.97 Å).[16] A similar stabilization of the $AlMe_2^+$ cation by polycyclic ethers was found in the two complexes $[AlMe_2{\cdot}[18]crown\text{-}6][AlMe_2Cl_2]$ and $[AlMe_2{\cdot}[15]crown\text{-}5][AlMe_2Cl_2]$.[17] In the first, the $AlMe_2$ fragment solvated with three oxygen atoms is bent while in the latter $AlMe_2$ fragment is linear due to solvation with five oxygen atoms.[17]

The isolation of the dimer $[H_2Al(\mu\text{-}H){\cdot}NMe_3]_2$[13] and monomeric complexes containing $[AlH_2L_n]^+$ cations[12] confirms the proposals of authors of earlier publications concerning the existence of both dimerization and autocomplexation processes (eq 3).[18,19]

$$L{\cdot}H_2Al(\mu\text{-}H)_2AlH_2{\cdot}L \overset{L}{\rightleftharpoons} 2AlH_3{\cdot}L \rightleftharpoons [AlH_2{\cdot}L_4][AlH_4] \quad (3)$$

Since the measurements of molecular weights of alanes $AlH_3{\cdot}L$ (L = NR_3, THF)[20-22] had given a value for the degree of association close to 1 (except for L = NMe_3),[21] it may be assumed that in the most cases the equilibrium of reaction 3 is shifted toward a monomer. Only the introduction of specific ligands (e.g. multidentate amines) into the system or availability of a suitable counterion results in the stabilization of dimeric or ionic forms of alane. In the present case, the AlH_2^+ cation is solvated by a relatively weak Lewis base and its stabilization is apparently conditioned by the joint packing with the bulky anion $[Cp_3Yb(Na)YbCp_3]^-$.

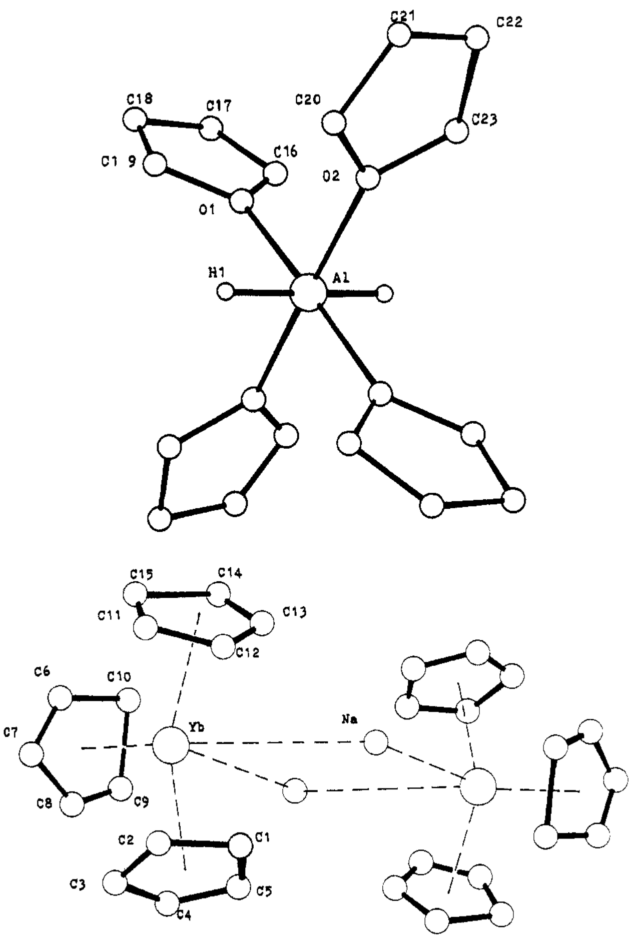

Figure 1. Structures of the cation $[AlH_2(OC_4H_8)_4]^+$ (a, top) and anion $[(\eta^5\text{-}C_5H_5)_3Yb(\mu\text{-}Na)Yb(\eta^5\text{-}C_5H_5)_3]^-$ (b, bottom) in complex **1** (two statistically occupied positions for Na atoms are shown).

It should be noted that anion **1a** is unique in that it is a complex particle consisting of two Cp_3Yb^- anions and the Na^+ cation bound by ionic interactions. The structure of the Cp_3Yb moieties is close to the structure of this fragment in molecular complexes $Cp_3M{\cdot}L$[23] and in the anion $[(C_5H_4CMe_3)_3Sm]^-$ in $Na[Cp'_3Sm]{\cdot}THF$ (**3**):[24] two C_5 pentagons are oriented in the same direction with respect to Yb–Na axis, but the third one is in the opposite direction. Taking into account the difference in ionic radii of the metals, the mean Yb–C distance in **1a** is noticeably less than that in **3**[24] but is comparable with the Yb–C_{av} value in the covalent $[Cp_2Yb(\mu\text{-}H)]_2[(\mu\text{-}H)AlH_2{\cdot}N(C_2H_5)_3]_2{\cdot}C_6H_6$ complex (2.60 Å).[25]

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Table 4. Main Geometric Characteristics of the $[Cp_3M(\mu\text{-}X)MCp_3]^-$ Anions

anion	M–C, Å	M··X, Å	M··M, Å	MXM′, deg	CpMCp, deg	ΣS_L		ref
						Cp_3M	real	
$[Cp_3Yb(Na)YbCp_3]^-$ (**1**)	2.63	3.54 3.60	6.72	140.4	352.6	0.89	0.96	this work
$[Cp_3Sm(Cl)SmCp_3]^-$ (**4a**)	2.74	3.70 3.77	6.48	120.2	355.8	0.82	0.89	23
$[Cp_3Sm(Cl)SmCp_3]^-$ (**4b**)	2.76	2.80 2.83	5.39	146.5		0.81	0.92	26
$[Cp_3U(Cl)UCp_3]^-$ (**5**)	2.79	2.79 2.82	5.50	156.5	351	0.79	0.90	27
$[Cp_3U(H)UCp_3]^-$ (**6**)	2.82	2.0 2.4	4.40	160		0.77	0.85	28
$[Cp'_3U(H)UCp'_3]^-$ (**7**)	2.84		4.46		357.1	0.76	0.83	29
$[Cp_3Nd(H)NdCp_3]^-$ (**8**)	2.81	2.2	4.40	180		0.78	0.85	30
$[Cp_3Lu(H)LuCp_3]^-$ (**9**)	2.71	2.1	4.18	180	352.1	0.84	0.92	31
$[Cp'_3U(Me)UCp'_3]^-$ (**10**)	2.82	2.71 2.74	5.45	176.9	351	0.77	0.88	32

Complex anion **1a** is stoichiometrically similar to the recently documented $[Cp_3Sm(\mu\text{-}Cl)SmCp_3]^-$ anion isolated as salts with $[LiEt_2O)_2]^+$ (**4a**)[23] and $[Li(DME)_2]^+$ (**4b**)[24] cations. The analogous anions of uranium, neodymium, and lutetium containing bridging chlorine, hydrogen, and methyl ligands $[Cp_3U(\mu\text{-}Cl)UCp_3]^-$ (**5**),[27] $[Cp_3U(\mu\text{-}H)UCp_3]^-$ (**6**),[28] $[(C_5H_4SiMe_3)_3U(\mu\text{-}H)U(C_5H_4SiMe_3)_3]^-$ (**7**),[29] $[Cp_3Nd(\mu\text{-}H)NdCp_3]^-$ (**8**),[30] $[Cp_3Lu(\mu\text{-}H)LuCp_3]^-$ (**9**),[31] $[(C_5H_4Me)_3U(\mu\text{-}CH_3)U(C_5H_4Me)_3]^-$ (**10**)[32] have been described as well. In the crystal structure of **1a**, the sodium atoms statistically occupy two positions connected by a center of symmetry (Figure 1b). The analogous phenomenon was observed in the structures of **5** and **6**[27,28] and proposed for complex **10**.[32] A bridge atom in the above anions binds two atoms of the f element in a complex. The M–X–M angles change from 120.2° in **4a** to 176.9° in **10** (Table 4), though, in the latter case, a probable disorder of bridge ligands can increase this value.[32] The Yb···Na distance is sufficiently large that this interaction can be considered as a purely ionic one. Nevertheless, the Na^+ cation and bridge ligands Cl, H, and CH_3 effectively shield the $(\eta^5\text{-}C^5H_5)_3Yb$ fragment, noticeably increasing the degree of metal coordination sphere filling $S_L = \sum(S_i/r_i^2)$,[33] where $S_{\eta}{}^5\text{-}C_5H_5 = 2.05$, $S_{Cl} = 0.9$, $S_H = 0.37$, and $r_i = r_{M\text{-}C}$ or $r_{M\text{-}X}$ (Table 4). Consequently, in complex **1**, a new type of stabilization of the coordinately unsaturated $(\eta^5\text{-}C_5H_5)_3M$ fragment by ionic metal–metal bonding has been demonstrated, in addition to the known solvation by a Lewis base, coordination of neutral and anionic bridge ligands, and formation of contact van der Waals dimers.[34]

In conclusion, it should be noted that the stability of mononuclear Cp'_3Ln^- anions depends on the steric and electronic properties of the cyclopentadienyl ligand and varies according to the series $Cp_3Ln^- < Cp'_3Ln^- \gg Cp''_3Ln^- \sim Cp^*_3Ln^-$, whereas for neutral Cp'_3Ln molecules, the compounds containing Cp″ ligands are the most stable. In particular, reaction of CpNa with LnI_2 (Ln = Sm, Yb) results in formation of an $NaCp_3Ln$ ate complex as the primary product when any ratio of reactants is used, and to isolate Cp_2Ln metallocenes, it is necessary to decompose the ate complex. At the same time, the analogous reaction involving $C_5H_3{}^tBu_2Na$ directly yields the related $Cp''_2Ln\cdot L$ metallocenes.

Supplementary Material Available: Listings of anisotropic temperature factors and hydrogen coordinates and isotropic temperature factors (2 pages). Ordering information is given on any current masthead page.

OM930740Z

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