Unusual .eta.6-toluene coordination to an alkali metal. X-ray crystal structure of organolutetium complex Lu{CH(SiMe3)2}3(.mu.-Cl)K(.eta.6-C7H8)2 and the solubilization of unsolvated alkali-metal halides in hydrocarbon media

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$(I)[CO]^{1.8}[H_2]^{0.7}[33DMB]_0^{0.1}$ completely controls the development of the active hydroformylation system.

$$[RCORh(CO)_4]_t = 4[Rh_4(CO)_{12}]_0 \times (1 - \exp(-k_0(I)[CO]^{1.8}[H_2]^{0.7}[33DMB]_0^{0.1}t)) \quad (21)$$

In conclusion, this study has presented a systematic approach for decoupling induction and steady-state kinetics for the unmodified rhodium catalyzed hydroformylation reaction. The present analysis illustrates the usefulness of treating, as far as possible, the precatalytic and catalytic reaction sequences individually. Without proving that the transformation of a precursor has occurred, or even to what degree it has occurred, it is difficult to accurately speak of the activation energies and the reaction orders associated with the steady-state kinetics of a catalytic cycle. Even though only induction and steady-state kinetics appear in this particular homogeneously catalyzed reaction, it is possible to broaden the context, and to include deactivation as well. The inclusion of deactivation kinetics into the present approach is straightforward. Such a case, where induction, steady-state kinetics, and deactivation all appear and can be decoupled from the overall dynamics, has already been treated.[22,23]

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Supplementary Material Available: A typical in situ infrared spectrum of $Rh_4(CO)_{12}$, CO, and 3,3-dimethylbut-1-ene in *n*-hexane prior to the addition of hydrogen, a plot of $k_{obs}(I)$ as a function of the 3,3-dimethylbut-1-ene concentration, a plot of $RCORh(CO)_4$ as a function of the liquid phase concentration of hydrogen and as a function of time, and a plot of $RCORh(CO)_4$ as a function of temperature and as a function of time (3 pages). Ordering information is given on any current masthead page.

Unusual η^6-Toluene Coordination to an Alkali Metal. X-ray Crystal Structure of $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(\eta^6\text{-}C_7H_8)_2$ and the Solubilization of Unsolvated Alkali-Metal Halides in Hydrocarbon Media

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Reaction of $Lu\{CH(SiMe_3)_2\}_3$ (**1**) with KCl in ether, or reaction of $LuCl_3$ with $KCH(SiMe_3)_2$ (3 equiv) in ether, affords $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(ether)$ (**2**). Coordinated ether is readily removed from **2** under vacuum to afford $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K$ (**3**), which contains coordinated KCl that is not stabilized by a donor ligand. Reaction of **1** with KBr yields $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Br)K(ether)$ (**4**), which can be converted to $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Br)K(C_7H_8)$ (**5**). Dissolution of **3** in toluene affords $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(C_7H_8)_2$ (**6**). Stepwise removal of coordinated toluene from **6** can be achieved, first to give the mono(toluene) adduct $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(C_7H_8)$ (**7**), and finally to **3**. Compound **6** crystallizes in space group $P\bar{1}$ (No. 2), with $a = 12.0060$ (12) Å, $b = 13.9624$ (14) Å, $c = 16.5370$ (42) Å, $\alpha = 105.44$ (4)°, $\beta = 99.77$ (7)°, $\gamma = 106.27$ (10)°, $V = 2474$ Å^3, and $Z = 2$. The current $R = 0.051$ and $R_w = 0.061$ for 6445 independent reflections with $I > 2.5\sigma(I)$. **6** shows unusual η^6 coordination of both toluenes to potassium. In contrast, neither $La\{CH(SiMe_3)_2\}_3$ nor $Lu(C_5Me_5)_2CH(SiMe_3)_2$ reacts with KCl in ether.

Introduction

Salt coordination is a ubiquitous, if undesirable, phenomenon in organolanthanide chemistry,[1] arising as a consequence of general synthetic procedures involving alkylation. Removal of this coordinated salt often necessitates an ingenious sequence of reactions.[2] Coordination of an alkali-metal halide to an electron-deficient lanthanide is invariably associated with its stabilization by a donor ligand such as ether, THF, or a chelating amine. In addition, the solubilization of alkali-metal salts in hydrocarbon media by in situ methods has been the subject of considerable recent attention,[3] direct dissolution of $(MX)_\infty$ with nonmacrocyclic ligands not always being successful, due to difficulties associated with the aggre-

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$$\underset{\mathbf{3}}{\mathrm{LuR_3(\mu\text{-}Cl)K}} + \text{toluene} \longrightarrow \underset{\mathbf{6}}{\mathrm{LuR_3(\mu\text{-}Cl)K(\eta^6\text{-}C_7H_8)_2}}$$

Figure 1.

gated, extant, infinite lattice.

In this contribution we report the preparation of the unsolvated alkali-metal halides Lu{CH(SiMe$_3$)$_2$}$_3$(μ-X)K (X = Cl, Br) by direct adduct formation of KX with Lu{CH(SiMe$_3$)$_2$}$_3$. The X-ray crystal structure of Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(η^6-toluene)$_2$ displays η^6 coordination of both toluenes to an alkali metal.

Results and Discussion

We rationalized that an electrophilic organolanthanide possessing large, flexible alkyl groups could form a stable adduct with an unsolvated alkali-metal halide. A suitable candidate is Lu{CH(SiMe$_3$)$_2$}$_3$,[4] thus avoiding heteroatoms capable of prior coordination to the alkali metal. Addition of Lu{CH(SiMe$_3$)$_2$}$_3$ (1) to a stirred ether suspension of KCl (5 equiv) led cleanly to Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(ether) (2). It is remarkable that coordination of KCl to 1 (and to ether) overcomes the energy of the KCl lattice, thus enabling its dissolution (eq 1).

$$\underset{1}{\mathrm{Lu\{CH(SiMe_3)_2\}_3}} + \mathrm{KCl} \rightarrow \underset{2}{\mathrm{Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(ether)}} \quad (1)$$

Coordinated ether is readily removed by heating solid 2 (70 °C, 2 h, 10^{-2} mmHg) to afford Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K (3), which contains coordinated KCl that is not stabilized by a donor ligand. Compound 3 may adopt a weakly bridged polymeric structure in order to effect stabilization of the unsolvated potassium. It is interesting that this polymer is readily broken up to give hydrocarbon-soluble monomeric species through facile adduct formation to potassium with relatively weakly coordinating solvents such as ether (to give 2), and with aromatics such as toluene to give 6 (vide infra). Coordination of KCl to the Lu{CH(SiMe$_3$)$_2$}$_3$ fragment of 3 does not perturb the methyne or SiMe$_3$ ^{1}H NMR chemical shifts of 3 in C$_6$D$_{12}$ from those in Lu{CH(SiMe$_3$)$_2$}$_3$ (1). Characterization of 3 was achieved by low-temperature (to minimize the chance of decomposition) ^{13}C NMR spectroscopy in CD$_2$Cl$_2$ and by solid-state ^{13}C CPMAS spectroscopy, as well as elemental analysis. In the ^{13}C NMR spectrum of 3 (CD$_2$Cl$_2$, −80 °C), the methyne and SiMe$_3$ groups are magnetically equivalent at δ 51.31 (J_{CH} = 91 Hz) and δ 3.74, respectively; KCl does not appear to induce time-averaged asymmetry into the CH(SiMe$_3$)$_2$ groups in solution, even at −80 °C. The ^{13}C NMR CPMAS solid-state NMR spectrum of 3 does, however, indicate asymmetry imposed into the CH(SiMe$_3$)$_2$ groups by coordination of KCl to Lu{CH(SiMe$_3$)$_2$}$_3$.[5]

In a similar manner, it is possible to prepare a KBr adduct by reaction of Lu{CH(SiMe$_3$)$_2$}$_3$ (1) with KBr in ether, to afford Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Br)K(ether) (4).

$$\underset{1}{\mathrm{Lu\{CH(SiMe_3)_2\}_3}} + \mathrm{KBr} \rightarrow \underset{4}{\mathrm{Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Br)K(ether)}} \quad (2)$$

Table I. Crystal Data and Data Collection Parameters for Compound 6

(a) Crystal Data	
chem formula	C$_{35}$H$_{73}$ClKSi$_6$Lu
mol wt	912.0
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	12.0060 (12)
b, Å	13.9624 (14)
c, Å	16.5370 (42)
α, deg	105.44 (4)
β, deg	99.77 (7)
γ, deg	106.27 (10)
V, Å^3	2474
Z	2
D_{calcd}, g cm^{-3}	1.224
F(000), e	948
μ(Cu Kα), cm^{-1}	65.86
approx cryst dimens, mm	0.63 × 0.5 × 0.38
(b) Data Collection	
check reflns	(−1,1,3), (210)
cryst decay during data collection, %	<2
$\theta/2\theta$ range, deg	2.5 < θ < 60.0
scan method	$\theta/2\theta$
max time/reflns, s	30
total data	7333
total unique data	7212
obsd $I > 2.5\sigma(I)$	6445
(c) Refinement	
no. of refined params	326
weighting factor, g	0.0 (unit weights)
R	0.051
R_w	0.061
goodness of fit, S	2.5
min/max residual densities in final Fourier map, e/Å^3	0.8/−1.3

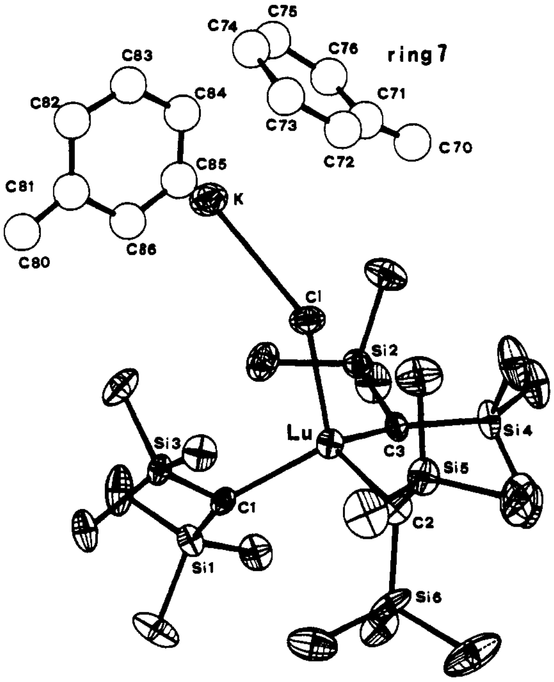

Figure 2. Perspective view of Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(C$_7$H$_8$)$_2$ (6). Only the major toluene occupants are shown.

Although 3 is insoluble in hexane, dissolution in aromatic solvents such as toluene affords Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(C$_7$H$_8$)$_2$ (6) (Figure 1). The X-ray structure of Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(C$_7$H$_8$)$_2$ (6) was determined to investigate the unusual stabilizing coordination of toluene to potassium. A summary of the crystal data and the structure analysis are given in Table I, positional parameters in Table II, and important bond distances and angles in

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Table II. Positional Parameters and Their Estimated Standard Deviations for Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(C$_7$H$_8$)$_2$ (6)[a]

atom	*x*	*y*	*z*	10^3U, Å^2
Lu	0.8107 (1)	0.2043 (1)	0.24025 (9)	46.9 (3)
Cl	0.6981 (7)	0.0085 (6)	0.1878 (5)	79 (2)
K	0.4893 (7)	−0.1655 (6)	0.1947 (5)	101 (3)
Si(1)	0.6818 (7)	0.3900 (7)	0.3749 (6)	70 (2)
Si(2)	0.9028 (7)	0.1544 (7)	0.4320 (6)	71 (3)
Si(3)	0.5265 (7)	0.2214 (6)	0.1944 (5)	59 (2)
Si(4)	1.1050 (8)	0.2093 (7)	0.3397 (6)	72 (3)
Si(5)	0.8827 (8)	0.1789 (7)	0.0272 (6)	76 (3)
Si (6)	0.9446 (8)	0.4086 (7)	0.1596 (6)	73 (3)
C(1)	0.677 (2)	0.294 (2)	0.267 (2)	43 (6)
C(2)	0.907 (2)	0.265 (2)	0.142 (2)	55 (7)
C(3)	0.963 (2)	0.226 (2)	0.361 (2)	57 (8)
C(11)	0.661 (3)	0.516 (3)	0.361 (2)	109 (12)
C(12)	0.558 (3)	0.330 (3)	0.427 (2)	116 (13)
C(13)	0.833 (2)	0.439 (2)	0.461 (2)	67 (8)
C(21)	0.740 (3)	0.147 (3)	0.430 (2)	102 (12)
C(22)	0.901 (3)	0.012 (2)	0.396 (2)	95 (11)
C(23)	0.991 (3)	0.221 (2)	0.552 (2)	84 (10)
C(31)	0.541 (2)	0.158 (2)	0.079 (2)	70 (9)
C(32)	0.423 (3)	0.299 (2)	0.175 (2)	95 (11)
C(33)	0.442 (3)	0.111 (2)	0.231 (2)	95 (11)
C(41)	1.204 (3)	0.332 (2)	0.323 (2)	88 (10)
C(42)	1.208 (3)	0.187 (3)	0.432 (2)	102 (12)
C(43)	1.072 (3)	0.094 (2)	0.236 (2)	90 (10)
C(51)	0.832 (3)	0.032 (2)	0.014 (2)	82 (10)
C(52)	0.773 (3)	0.206 (3)	−0.055 (2)	110 (12)
C(53)	1.030 (3)	0.203 (3)	−0.010 (2)	133 (15)
C(61)	0.990 (2)	0.484 (2)	0.280 (2)	70 (9)
C(62)	0.817 (3)	0.446 (3)	0.106 (2)	108 (12)
C(63)	1.078 (3)	0.469 (3)	0.118 (2)	125 (14)
C(70)	0.813 (2)	0.770 (2)	0.192 (2)	146 (16)
C(71)	0.682 (2)	0.706 (1)	0.156 (1)	91 (11)
C(72)	0.621 (2)	0.697 (2)	0.073 (1)	111 (13)
C(73)	0.498 (2)	0.637 (2)	0.040 (1)	118 (14)
C(74)	0.436 (2)	0.587 (2)	0.090 (2)	131 (15)
C(75)	0.497 (2)	0.597 (2)	0.174 (2)	128 (15)
C(76)	0.620 (2)	0.657 (2)	0.207 (1)	137 (16)
C(80)	0.24 (1)	0.92 (2)	0.315 (6)	199 (23)
C(81)	0.321 (6)	0.860 (6)	0.338 (3)	101 (12)
C(82)	0.282 (5)	0.750 (6)	0.312 (1)	91 (11)
C(83)	0.36 (1)	0.699 (3)	0.334 (4)	118 (14)
C(84)	0.48 (1)	0.76 (1)	0.381 (4)	155 (17)
C(85)	0.521 (2)	0.87 (1)	0.407 (2)	107 (13)
C(86)	0.444 (8)	0.922 (3)	0.384 (2)	97 (11)
C(701)	0.378 (3)	0.538 (3)	0.081 (2)	114 (13)
C(711)	0.508 (3)	0.612 (2)	0.108 (2)	90 (10)
C(721)	0.554 (2)	0.662 (2)	0.051 (2)	71 (9)
C(731)	0.674 (2)	0.731 (2)	0.075 (2)	60 (8)
C(741)	0.749 (3)	0.751 (2)	0.158 (2)	90 (10)
C(751)	0.704 (3)	0.701 (2)	0.215 (2)	82 (10)
C(761)	0.584 (2)	0.632 (2)	0.191 (2)	55 (7)
C(801)	0.098 (4)	0.736 (4)	0.236 (3)	205 (22)
C(811)	0.228 (2)	0.791 (2)	0.291 (2)	54 (7)
C(821)	0.296 (2)	0.730 (2)	0.314 (2)	74 (9)
C(831)	0.416 (3)	0.780 (3)	0.365 (2)	120 (13)
C(841)	0.468 (2)	0.891 (2)	0.394 (2)	67 (8)
C(851)	0.400 (2)	0.952 (2)	0.372 (2)	68 (8)
C(861)	0.280 (3)	0.902 (3)	0.320 (2)	107 (12)

[a] C(70)–C(76) and C(80)–C(86) are the major occupants of toluene rings 7 and 8, respectively, with C(701)–C(761) and C(801)–C(861) being their minor occupants.

Table III. The molecular structure (Figure 2) shows unusual η^6 coordination of toluene to potassium with K–M7 = 3.003 Å and K–M8 = 3.128 Å (M7 and M8 are the centroids of the toluene rings). Although the structural consequences of toluene coordination in 6 are not complicated by additional ligands bound to the alkali metal, in addition to the difference in K–ring centroid distances, the coordination of the two toluenes to potassium also shows asymmetry with respect to the Cl–K bond with Cl–K–M7 = 127.8°, Cl–K–M8 = 98.0°, and M7–K–M8 = 109.2°. The reason for this difference is unknown, but we suspect that very little energy is required to perturb this aspect of toluene coordination to potassium, presumably dominated by nonbonding interactions or crystal-packing forces.

Table III. Relevant Bond Lengths (Å) and Angles (deg) for Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(C$_7$H$_8$)$_2$ (6)

	Bond Lengths		
Lu–C(1)	2.324 (10)	C(2)–Si(5)	1.885 (8)
Lu–C(2)	2.349 (10)	C(2)–Si(6)	1.85 (1)
Lu–C(3)	2.357 (8)	C(3)–Si(2)	1.85 (1)
Lu–Cl	2.515 (2)	C(3)–Si(4)	1.86 (1)
Cl–K	3.004 (4)	K–M7[a]	3.003
C(1)–Si(3)	1.826 (7)	K–M8[a]	3.128
C(1)–Si(1)	1.908 (9)		
	Bond Angles		
Lu–Cl–K	145.9 (1)	Lu–C(2)–Si(6)	115.5 (5)
C(1)–Lu–Cl	109.2 (2)	Lu–C(3)–Si(2)	111.5 (4)
C(2)–Lu–Cl	114.7 (2)	Lu–C(3)–Si(4)	117.2 (5)
C(3)–Lu–Cl	102.5 (2)	Si(1)–C(1)–Si(3)	114.3 (5)
C(1)–Lu–C(2)	107.0 (4)	Si(5)–C(2)–Si(6)	115.8 (5)
C(1)–Lu–C(3)	116.8 (3)	Si(2)–C(3)–Si(4)	113.6 (6)
C(2)–Lu–C(3)	106.8 (3)	Cl–K–M7	127.8
Lu–C(1)–Si(1)	127.3 (4)	Cl–K–M8	98.0
Lu–C(1)–Si(3)	112.2 (4)	M7–K–M8	109.2
Lu–C(2)–Si(5)	122.5 (4)		

[a] M7 and M8 are the centroids of the toluene rings.

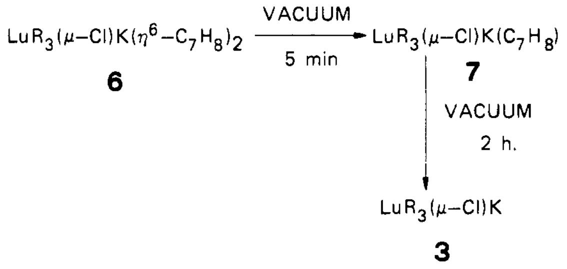

Figure 3.

In polymeric KC$_5$H$_4$SiMe$_3$[6] the K–ring centroid distance is 2.78 Å, while the shortest potassium–ring plane distance is 2.972 Å in fluorenylpotassium·TMEDA[7] (TMEDA = *N,N,N′,N′*-tetramethyethylenediamine) and 3.01 Å in K[PhCHPMe$_2$CHPh].[8] In these contact ion pairs, the essentially ionic interaction results in K–ring centroid distances slightly shorter than those seen in 6.

The η^6 coordination of toluene to the potassium of covalently bound KCl in 6 can best be regarded as an induced dipole interaction, though the mode of coordination still possesses predominantly ionic character (ionic radius: K$^+$, 1.33 Å; half van der Waals thickness of benzene ring,[9] 1.70 Å), the average K–ring carbon distances being 3.31 and 3.42 Å for the two toluenes in 6. The Cl–K distance of 3.005 (4) Å is, as expected, shorter than that in crystalline KCl (3.139 Å).[10] In contrast to the essentially linear Ln–X–Li unit in Ln{CH(SiMe$_3$)$_2$}$_3$(μ-X)Li(pmdeta) (pmdeta = *N,N′,N′,N″,N″*-pentamethyldiethylenetriamine) (Ln = La, X = Cl, 165°; Ln = Sm, X = Me, 174°),[11]

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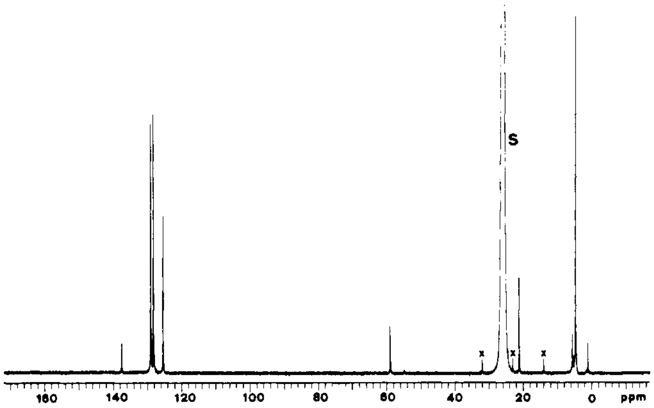

Figure 4. ^{13}C NMR spectrum of $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(C_7H_8)_2$ (6) (C_6D_{12}, 25 °C): X = hexane, S = C_6D_{12}. A trace of another $Lu\text{-}CH(SiMe_3)_2$-containing species, probably $Lu\{CH(SiMe_3)_2\}_3$, can be seen (δ 55.0, CH: δ 5.0, $SiMe_3$).

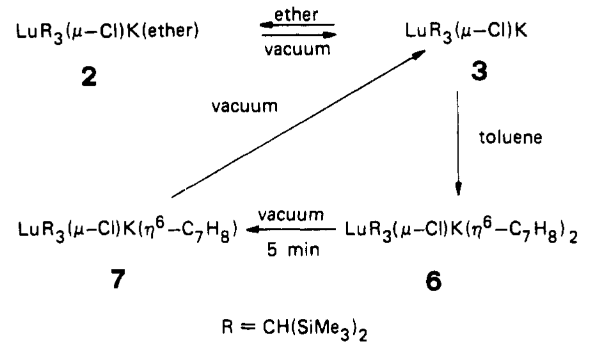

Figure 5.

the Lu-Cl-K unit in 6 is significantly perturbed from linearity with Lu-Cl-K = 145.9 (1)°.

Interestingly, it is possible to remove coordinated toluene in a selective and stepwise fashion to yield first the mono(toluene) adduct $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(C_7H_8)$ (7), by evacuation of 6 as a solid (25 °C, 10 min, 10^{-2} mmHg). Longer exposure to vacuum results in the complete loss of coordinated toluene to give 3 (Figure 3). The η^6 coordination of toluene to potassium in compounds 6 and 7 does not perturb the ^1H NMR chemical shift (in C_6D_{12}) of the coordinated toluene methyl resonance from that in free toluene, and there is no detectable ^1H NMR chemical shift difference (in C_6D_{12}) of this resonance between 6 and 7. However, the toluene integrated intensities are obviously different. Additionally, the ^{13}C chemical shifts of coordinated toluene in 6 measured in C_6D_{12} (Figure 4) are identical with those of free C_7H_8 in C_6D_{12} (see Experimental Section). Removal of C_6D_{12} under vacuum gave 7, providing evidence that toluene remains coordinated in solution. These results are summarized in Figure 5.

Although arenes are well-known to coordinate to low-valent transition metals[12a] and η^6-coordination to gallium,[12b] indium, and thallium to give inclusion compounds,[12c] as well as asymmetric exterior coordination to Ag^+ from deltaphane,[12d] and to lanthanides[13] has been found (with the electron-rich aromatics C_6Me_6 and 1,3,5-$C_6H_3{}^tBu_3$), only a few examples[14] are known in which a simple arene is π-bound to an alkali metal. However, the dianions $[(TMEDA)Li]_2$anthracenide,[15a] $[(TMEDA)Li]_2$-naphthalenide,[15b] and $[Na(THF)_2]_2[AlMe_2C_{14}H_{10}]_2$,[15c] prepared from the double deprotonation of the respective dihydro aromatic by *n*-BuLi, as well as $(C_5H_5)V(\mu_2\text{-}\eta^6\text{-}C_6H_6)Li(TMEDA)$[16] are best regarded as contact ion pairs, which are fundamentally different from the π-coordination of a neutral arene to a covalently bound potassium as seen in 6 and 7, an induced dipole interaction. Atwood[14] has prepared "liquid clathrates" by reaction of alkali-metal salts with excess $AlMe_3$ in the presence of an aromatic, especially benzene or toluene. A comparison of the range and average K···C distances for η^6 coordination of benzene and toluene in these compounds and in 6 is given in Table IV. Although quite a spread of individual K···C distances is observed (non-η^6-coordinated aromatics[14d] have been excluded from Table IV), their mean falls in a narrow range.

Table IV. Summary of K• • •C Interactions for η^6-Coordinated Aromatics

compd	range, Å	mean, Å	ref
$Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)\text{-}K(C_7H_8)_2$ (6)	3.21 (1)-3.38 (1) (ring 7) 3.24 (1)-3.56 (1) (ring 8)	3.31 3.42	
$K[AlMe_3NO_3]\cdot C_6H_6$	3.29 (1)-3.46 (1)	3.36	14a
$K[Al_7O_6Me_{16}]\cdot C_6H_6$	3.29 (1)-3.39 (2)	3.33	14c
[K(DB-18-crown-6)]-$[Al_2Me_6Cl]\cdot 2C_6H_6$	3.29 (2)-3.50 (3)	3.39	14d
[K(DB-18-crown-6)]-$[GaMe_3NCS]\cdot 2C_6H_6$	3.48 (1)-3.72 (1)	3.59	14d

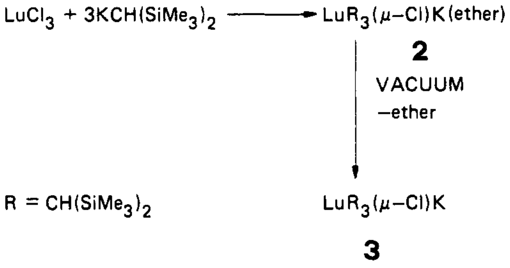

Figure 6.

Recent molecular orbital calculations[17] carried out on $[(C_6H_6)K]^+$ (C_{6v} symmetry) indicate no transfer of charge from C_6H_6 to K^+, suggestive of an induced dipole interaction. A very different situation was calculated for $[(C_6H_6)Ga]^+$ with a covalent interaction involving a dative bond between benzene and the potassium ion. Although K^+ has an ionic radius similar to that of Ga^+, the potassium 4s and 4p orbitals are too high in energy to allow significant bonding, overlap with the π-bonding orbitals of C_6H_6.

Preliminary ab initio calculations on the geometry of the Lu-Cl-K unit in 6 indicate that a shallow potential well exists for bending at chlorine, suggesting that steric, rather than electronic, influences are probably dominant in determining the geometry of the Lu-Cl-K(toluene)$_2$ unit in 6. Calculations were carried out with use of the GAMESS

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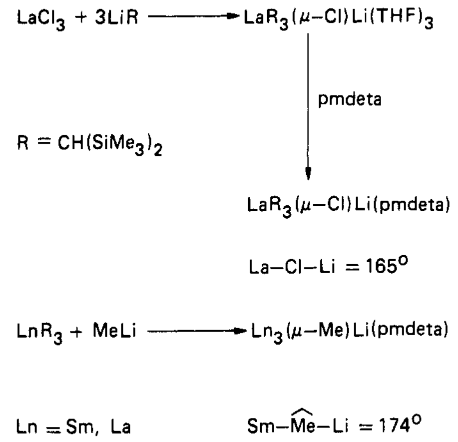

Figure 7.

program package. We chose to model the Lu–Cl–K fragment in **6** by Cl–Li–Cl–Li, this representing the simplest possible model. To keep the model neutral, lutetium was replaced by the fragment LiCl. We admit the inadequacy of such a model to represent **6** and the fact that the geometry of the Lu–Cl–K(toluene)$_2$ unit may reflect a difference in bonding character between LiX(pmdeta) and KCl(η^6-C_7H_8)$_2$ fragments, potassium being more polarizable and hence more susceptible to an induced dipole than lithium. Nevertheless, this model provides insight into the large difference in geometry observed between **6** and the closely related $Ln\{CH(SiMe_3)_2\}_3(\mu$-X)Li(pmdeta).[11]

In order to investigate the chemistry of η^6-coordinated toluene to an alkali metal, a more convenient synthesis and direct route to **2** was developed. Although a rapidly stirred suspension of $LuCl_3$ in ether reacts very slowly (days, 25 °C) with $LiCH(SiMe_3)_2$ (3 equiv) to give an inseparable mixture of several products, reaction of anhydrous $LuCl_3$ with $KCH(SiMe_3)_2$ (3 equiv) in ether afforded $Lu\{CH(SiMe_3)_2\}_3(\mu$-Cl)K(ether) (**2**) as the only product in 66% isolated yield, from which **3** is prepared as described above (Figure 6). This mode of reactivity is in contrast[1e,18] to that previously observed on alkylation of lanthanide trichlorides with $LiCH_2SiMe_3$ or $LiCH(SiMe_3)_2$ and highlights the advantages associated with the use of $KCH(SiMe_3)_2$ in ether. This obviates the need for THF as solvent, thus enabling the synthesis of solvent-free **3**, through the subsequent facile removal of coordinated ether, which binds much less strongly than THF.

Although similar coordination geometries at the lanthanide metal have been previously observed in $La\{CH(SiMe_3)_2\}_3(\mu$-Cl)Li(pmdeta)[11a] and $Sm\{CH(SiMe_3)_2\}_3(\mu$-Me)Li(pmdeta),[11b] the alkali metal is stabilized by coordination of a tridentate amine, rather than η^6-toluene (Figure 7). Note that adduct formation occurs exclusively at the alkali metal and not at the lanthanide. In contrast to this chemistry, we have used the $Lu\{CH(SiMe_3)_2\}_3$ fragment as a spectator Lewis acid and focused on the chemistry associated with the KX(toluene)$_n$ unit. Of particular interest is the fact that $Lu\{CH(SiMe_3)_2\}_3$ can function as a Lewis acid of a requisite size. The subtle influence of the lanthanide metal on the propensity for adduct formation is clearly demonstrated as, in contrast to the clean KCl adduct formation by $Lu\{CH(SiMe_3)_2\}_3$, the larger[19] lanthanide in $La\{CH(SiMe_3)_2\}_3$[4] does not react with excess KCl in ether. The coordination sphere around the metal center also has, as expected, a clear influence on the reactivity. Thus, although no reaction is observed between $Lu(C_5Me_5)_2CH(SiMe_3)_2$ and excess KCl in ether, Teuben[20] has reported that reaction of $Ce(C_5Me_5)_2CH(SiMe_3)_2$ with LiCl (2 equiv) in the presence of TMEDA resulted in metathesis of the Ce–$CH(SiMe_3)_2$ bond to afford $Ce(C_5Me_5)_2(\mu$-Cl)$_2$Li(TMEDA) and $LiCH(SiMe_3)_2$ (Figure 8).

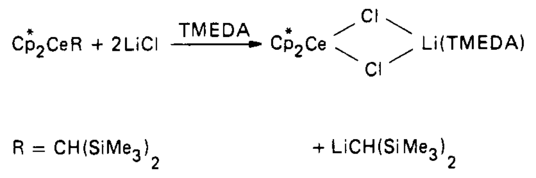

Figure 8.

Conclusions

We have demonstrated that toluene reacts with solvent-free **3** to give the bis(toluene) species **6** and that coordinated toluene can be removed in a clean and stepwise fashion to form **7** and then completely to give **3**. In addition, $Lu\{CH(SiMe_3)_2\}_3$ has been shown to react directly with alkali-metal halides KX (X = Cl, Br) in ether to form the adducts **2** and **4**, respectively, and lanthanide tris(alkyl) complexes $Ln\{CH(SiMe_3)_2\}_3$, can act as size-dependent Lewis acids.

The straightforward synthesis of **3** via $LuCl_3$ and $KCH(SiMe_3)_2$ and its ability to coordinate simple arenes allow ready access to a detailed examination of the chemistry of unsolvated alkali-metal halides. Competition experiments will allow the affinity of different arenes and other donor ligands for coordinated alkali-metal halides to be examined.

Experimental Section

All experiments were performed under an argon atmosphere with use of Schlenk type glassware or in a Braun single-station drybox equipped with a −40 °C refrigerator under a nitrogen atmosphere. Elemental analyses were performed at Analytische Laboratorien, Elbach, West Germany. Nuclear magnetic resonance spectra were recorded on Varian XL-200 or Varian VXR-300 spectrometers. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents at δ 7.15 (C_6D_5H), δ 1.20 ($C_6D_{11}H$), δ 2.10 ($C_6D_5CD_2H$), and δ 5.32 ($CHDCl_2$). Coupling constants are reported in hertz. Anhydrous $LuCl_3$ was purchased from Cerac via Micropure, Driebergen-Rijsenb., The Netherlands. Solvents were PA grade and were dried initially over sodium wire and then distilled from the appropriate drying reagent (sodium benzophenone ketyl for ether and THF; sodium for hexane and toluene) under argon prior to use. Deuterated solvents were dried over 4-Å molecular sieves. $Lu\{CH(SiMe_3)_2\}_3$ was prepared analogously to $La\{CH(SiMe_3)_2\}_3$.[4]

Preparation of $KCH(SiMe_3)_2$. The synthesis of **2** required $KCH(SiMe_3)_2$ in solid form so that stoichiometrically precise amounts of reagents could be employed. A 7.5-g (67.0-mmol) amount of KO^{t}Bu was added in small portions to a stirred suspension of 11.2 g (67.5 mmol) of $LiCH(SiMe_3)_2$ in 300 mL of hexane in the drybox. After a small amount of KO^{t}Bu had been added, a homogeneous clear solution was formed, presumably through formation of a soluble adduct. Addition of more KO^{t}Bu resulted in a white, flocculent precipitate. After all the KO^{t}Bu had been added, the suspension was stirred for 16 h and then removed from the drybox and filtered and hexane-insoluble $KCH(SiMe_3)_2$ washed with 3 × 100 mL of hexane to remove LiO^{t}Bu. This afforded 10.9 g (55.0 mmol) of $KCH(SiMe_3)_2$ as a white powder, yield 82%. Anal. Calcd for $C_7H_{19}Si_2K$: C, 42.36;

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Preparation of Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(OEt$_2$) (2). Finely ground KCl was dried by heating at 130 °C for 16 h under vacuum. In the drybox, 198 mg (2.65 mmol) of KCl was stirred in 35 mL of ether and 260 mg (0.383 mmol) of Lu{CH(SiMe$_3$)$_2$}$_3$ added. This suspension was stirred for 15 h at 20 °C and filtered and the ether removed under vacuum. ^{1}H NMR spectroscopy showed the clean and complete conversion of Lu{CH(SiMe$_3$)$_2$}$_3$ to **2**. ^{1}H NMR (C_6D_6): δ 3.35 (q, 4 H, ether), 1.003 (t, 6 H, ether), 0.551 (SiMe$_3$), −0.703 (CH).

Alternative Preparation of Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(OEt$_2$) (2). A 2.30-g (11.62-mmol) amount of KCH(SiMe$_3$)$_2$ dissolved in 30 mL ether was added over 2 min to 1.1 g (3.91 mmol) of LuCl$_3$ suspended in 30 mL of ether in a double Schlenk tube in the drybox. The solution was stirred overnight at 20 °C and filtered and the solvent removed in vacuo to give Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(OEt$_2$) (**2**).

Preparation of Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K (3). Compound **2** obtained as above was heated at 70 °C for 2 h under vacuum to give 1.9 g of **3**, overall yield 66%. Anal. Calcd for Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K (**3**), $C_{21}H_{57}ClLuKSi_6$: C, 34.66; H, 7.90; K, 5.37. Found: C, 33.44; H, 7.41; K, 6.47. This analysis was on unpurified material, as redissolution in ether or toluene gives adduct formation (compound **2** or **6**, respectively), and **3** is insoluble in hexane for recrystallization purposes. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 0.125 (SiMe$_3$), −1.153 (CH). ^{13}C NMR (CD_2Cl_2, −80 °C): δ 51.31 (d, 91 Hz, *C*H), 3.74 (q, 117 Hz, Si*Me*$_3$). ^{1}H NMR (C_6D_{12}, 25 °C): δ 0.046 (SiMe$_3$), −1.123 (CH).

For comparison the ^{1}H NMR spectrum of Lu{CH(SiMe$_3$)$_2$}$_3$ (**1**) is as follows: δ 0.044 (Si*Me*$_3$), −1.12 (C*H*) (C_6D_{12}, 25 °C); δ 0.308 (Si*Me*$_3$), −0.82 (C*H*) (C_6D_6, 25 °C).

Preparation of Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Br)K(ether) (4). A 0.191-g (0.293-mmol) amount of Lu{CH(SiMe$_3$)$_2$}$_3$ was added to a stirred suspension of 0.067 g (0.56 mmol) of KBr in 8 mL of ether. This was stirred for 2 h at 20 °C and the solution filtered to remove excess KBr. Removal of ether under vacuum afforded **7**, which was recrystallized from toluene/hexane. ^{1}H NMR (C_6D_6, 25 °C): δ 3.15 (q, ether), 0.94 (t, ether), 0.567 (SiMe$_3$), −0.65 (CH). Compound **6** is the only species formed, as determined by the ^{1}H NMR spectrum of the crude reaction mixture. No KCH(SiMe$_3$)$_2$ was observed, which would have arisen from metathesis of the Lu–CH(SiMe$_3$)$_2$ bond by KBr.

Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Br)K(toluene) (5). This was prepared analogously to **7**, by removal of ether under vacuum from **6**, followed by addition of toluene (1 equiv). ^{1}H NMR (C_6D_{12}, 25 °C): δ 6.89 (m, toluene), 2.10 (s, 3 H, Me), 0.033 (s, 54 H, Si*Me*$_3$), −1.155 (s, 3 H, C*H*). Anal. Calcd for $C_{28}H_{65}BrLuKSi_6$: C, 38.91; H, 7.58. Found: C, 38.56; H, 7.30.

Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(toluene)$_2$ (6). Recrystallization of **3** from toluene/hexane results in the formation of **6**. Because of the facile loss of one toluene from **6** to give **7**, the bis(toluene) adduct **6** can only be isolated by crystallizing from toluene/hexane and then allowing the crystals to dry in the drybox without exposure to vacuum. ^{1}H NMR (C_6D_{12}, 25 °C): δ 6.89 (m, toluene), 2.104 (s, 6 H, Me), 0.048 (Si*Me*$_3$), −1.21 (C*H*). ^{13}C NMR (C_6D_{12}, 25 °C): δ 137.64 (*C*–Me), 129.14 (*C*H), 128.35 (*C*H), 125.53 (C_{para}), 59.11 (*C*H), 21.33 (Me), 4.80 (Si*Me*$_3$). For comparison, the ^{13}C NMR chemical shifts of C_7H_8 in C_6D_{12} at 25 °C are as follows: δ 137.60 (*C*–Me), 129.10 (*C*H), 128.32 (*C*H), 125.51 (C_{para}), 21.31 (Me). Anal. Calcd for Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(C_7H_8)$_2$ (**6**), $C_{35}H_{73}ClLuKSi_6$: C, 46.09; H, 8.07; K, 4.29. Found: C, 45.99 (45.8); H, 7.84 (8.1); K, 4.84 (4.05). Figures in parentheses are repeat analyses of a different batch. ^{13}C NMR for **3** dissolved in C_7D_8, hence giving **3**·2C_7D_8 (25 °C): δ 54.00 (d, 90 Hz, *C*H), 6.704 (q, 117 Hz, Si*Me*$_3$).

Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(C_7H_8) (7). Compound **7** was prepared by evacuation of solid **6** (25 °C, 10 min, 10^{-2} mmHg). Anal. Calcd for Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K(C_7H_8) (**7**), $C_{28}H_{65}ClLuKSi_6$: C, 41.02; H, 7.99; K, 4.77. Found: C, 41.30; H, 7.81; K, 4.51. The ^{1}H NMR spectrum is identical with that of **6** except for the integrated intensity of the toluene resonances.

X-ray Structure Analysis for 6. Single crystals of **6** were mounted under nitrogen in thin-walled glass capillaries in a drybox and held in place with use of silicone grease. All diffraction experiments were carried out at 195 K on an Enraf-Nonius CAD-4 four-circle diffractometer using graphite-monochromated Cu Kα radiation (λ = 1.5418 Å). Unit cell dimensions were determined from 23 centered reflections in the range 70.0° < 2θ < 79.3°. A total of 7333 diffracted intensities were measured in a unique hemisphere of reciprocal space ($-13 < h < 13$, $-15 < k < 15$, $0 < l < 18$) for 5.0° < 2θ < 120.0° by $\theta/2\theta$ scans. Details of the crystal data collection and reduction are given in Table I. The statistical absorption correction was performed by the Walker and Stuart method with the program DIFABS[21] (correction range 0.662–1.407). Structure solution was by direct methods and difference Fourier and refinement by block-diagonal least squares with unit weights w ($g = 0$ with $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics). All hydrogen atoms were assigned idealized geometries (C–H = 1.09 Å, H–C–H = 109.5°) and fixed isotropic displacement parameters.

Refinement of the major toluene occupant, without any positional constraints, gave K–ring carbon distances in the range 3.21 (1)–3.38 (1) Å for C71–C76 (K–(ring 7) = 3.38, 3.32, 3.29, 3.21, 3.29, 3.34 Å; average 3.31 (1) Å) and rather more variable distances for C81–C86, 3.24–3.56 Å (K–(ring 8) = 3.37, 3.56, 3.57, 3.47, 3.30, 3.25 Å; average 3.42 (1) Å). As both coordinated toluenes were rotationally disordered over two sites, some of the carbon atoms of the coordinated toluenes were poorly resolved with large thermal parameters; hence, a model including constraints (C–C = 1.400 Å, ∠C–C–C = 120 ± 1°) was applied by using HEXGNL in the XTAL program with the toluene carbon atoms being refined isotropically. The occupancy factors were calculated independently for both sets of "ring 7" and for "ring 8" toluenes and were in good mutual agreement. Calculated occupancy factors are as follows: ring C70–C76, 0.773 (1); ring C80–C86, 0.758 (1); ring C701–C761, 0.214 (5); ring C801–C861, 0.235 (7). The sum of calculated occupancy factors for ring 7 is 0.987, and the sum for ring 8 is 0.993. Only the major contributor to each toluene is shown. Final difference electron density maps show their largest features near the lutetium atom. All calculations were carried out with XTAL software.[22]

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Supplementary Material Available: Listings of anisotropic thermal parameters and bond distances and angles (3 pages); a table of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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