from thermolysis of $(C_5H_4R)_2Y(CH_2SiMe_3)(THF)$ and $(C_5H_5)_2YbCH_3/LiCl(THF)_n$ and from the reaction of $LiOCH{=}CH_2$ with $[(C_5H_4R)_2LnCl]_2$ are the dimeric lanthanide enolates $[(C_5H_4R)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$. With full characterization of these enolates in hand, formation of organolanthanide enolates in other systems should be readily observable via the distinctive enolate ^1H NMR pattern. Enolate formation should be considered as a possible competing side reaction when lanthanide alkyls are used in THF under harsh conditions.

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Registry No. **1**, 101953-51-9; **2**, 101979-21-9; **3**, 101953-52-0; **4**, 101953-53-1; $[(C_5H_5)_2LuCl]_2$, 78953-89-6; $LiOCH{=}CH_2$, 2180-63-4; $[(C_5H_5)_2YbCl]_2$, 12128-90-4; $[(C_5H_5)_2YCl]_2$, 57398-67-1; $[(CH_3C_5H_4)_2YCl]_2$, 80642-81-5; $(CH_3C_5H_4)_2Y(CH_2SiMe_3)(THF)$, 99593-37-0; $(C_5H_5)_2Y(CH_2SiMe_2)(THF)$, 99583-14-9.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

Organometallic Compounds of the Lanthanides. 36.[1] Bis(pentamethylcyclopentadienyl) Halide and Alkyl Derivatives of the Lanthanides

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The trichlorides of lanthanum and the lanthanides react with NaC_5Me_5 or KC_5Me_5 in tetrahydrofuran in the presence of ether or dimethoxyethane (dme) with formation of bis(pentamethylcyclopentadienyl)lanthanide halogen complexes of the types $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Na(Et_2O)_2$ (Ln = Pr, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Na(dme)_2$ (Ln = Pr, Gd, Tb, Dy, Ho, Er, Tm), and $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2K(dme)_2$ (Ln = La, Ce). The reactions of these organolanthanide halide complexes with CH_3Li or Me_3SiCH_2Li in the presence of dme or *N,N,N′,N′*-tetramethylethylenediamine (tmed) yield $(C_5Me_5)_2Lu(\mu\text{-}CH_3)_2Li(THF)_2$, $(C_5Me_5)_2Ln(\mu\text{-}CH_3)_2Li(tmed)$ (Ln = La, Pr, Lu), and $[Li(dme)_3][(C_5Me_5)_2Ln(CH_2SiMe_3)_2]$ (Ln = Pr, Lu), respectively. The new compounds have been characterized by elemental analyses and IR and NMR spectra. The structure of $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$, which has two slightly different independent molecules per asymmetric unit, has been elucidated through complete X-ray analysis. The crystals are orthorhombic with $a = 16.032\ (11)$ Å, $b = 16.503\ (6)$ Å, $c = 25.084\ (9)$ Å, space group $P2_1ca$, $D(\text{calcd}) = 1.372\ \text{g cm}^{-3}$, and $R = 0.0476$, for 3240 observed reflections with $I \geq 3\sigma(I)$.

Introduction

Organolanthanides of the type $(C_5H_5)_3Ln$ have been synthesized for all lanthanide metals and for the group IIIB (3[41]) metals scandium, yttrium, and lanthanum. However, dicyclopentadienyllanthanide halides were until recently only known for the heavier lanthanide metals.[2] Using the pentamethylcyclopentadienyl group as a bulky, substituted cyclopentadienyl ligand, Wayda and Evans[3] as well as Tilley and Andersen[4] succeeded for the first time in preparing bis(pentamethylcyclopentadienyl) derivatives of neodymium. Extensive investigations on this class of compounds, including X-ray structural determinations, have been carried out with some bis(pentamethylcyclopentadienyl)ytterbium halides[5-9] as well as some scandium,[10] yttrium,[11,12] samarium,[4] and lutetium analogues.[6,13] Only a few bis(pentamethylcyclopentadienyl)lanthanide alkyl or aryl compounds are in the literature, e.g., $(C_5Me_5)_2ScCH_3$,[10] $(C_5Me_5)_2ScC_6H_5$,[10] $(C_5Me_5)_2ScCH_2C_6H_5$,[10] $(C_5Me_5)_2YCH(SiMe_3)_2$,[12] $(C_5Me_5)_2YC_6H_5$,[12] $(C_5Me_5)_2SmC_6H_5(THF)$,[16] $(C_5Me_5)_2Yb(CH_3)_2Li(Et_2O)_2$,[5] $(C_5Me_5)_2LuCH_3$,[13,14] $(C_5Me_5)_2LuC_6H_5$,[13] $(C_5Me_5)_2LuCH_2SiMe_3$,[13] and $(C_5Me_5)_2Lu(CH_2)_2PMe_2$.[15] Only four of

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them, $(C_5Me_5)_2ScCH_3$,[10] $(C_5Me_5)_2LuCH_3$,[17] $(C_5Me_5)_2Lu(CH_2)_2PMe_2$,[15] and $(C_5Me_5)_2SmC_6H_5(THF)$,[16] were characterized by an X-ray structural analysis.

We have investigated the synthesis of the whole series of bis(pentamethylcyclopentadienyl)lanthanide chlorides and have succeeded in isolating and characterizing a number of alkali-metal halide adducts of these compounds including the La, Ce, and Pr derivatives. The synthesis and characterization of some bis(pentamethylcyclopentadienyl)lanthanide alkyl derivatives is also described.[18]

Experimental Section

All reactions and preparations were performed by using Schlenk tubes in an atmosphere of dried, oxygen-free argon. The solvents used were dried and freed of oxygen by refluxing and keeping over NaH or potassium and distilling under argon prior to use. Anhydrous rare-earth chlorides were prepared from the pure oxides (Auer-Remy, West Germany) by reaction with NH_4Cl.[19] Tetramethylethylenediamine (tmed) was dried and freed of oxygen by refluxing over KOH and followed by distillation under argon. Pentamethylcyclopentadiene, C_5Me_5H, was prepared according to a method described by Burger, Delay, and Mazenod.[20] Melting points were determined in sealed, argon-filled capillaries. Elemental analyses were performed on a Perkin-Elmer CHN-Analyzer 240 C. Reasonably satisfactory analyses could be obtained by using a special Schlenk tube and small aluminium cans for weighing these extremely sensitive compounds, but not in all cases because of their especially high sensitivity toward traces of moisture and air of some compounds. Metal analyses were carried out by complexometric titration against dithizone,[21] chlorine by titration with 0.1 N $AgNO_3$ solution, and lithium using a Perkin-Elmer 2380 atomic absorption spectrometer.

Infrared spectra were recorded as paraffin mulls between CsI plates, using a Perkin-Elmer 560 B (200–4000 cm^{-1}) spectrometer. Mass spectra were obtained on a Varian MAT 311 A. ^1H NMR spectra were obtained in sealed 5-mm tubes and ^{13}C NMR spectra in sealed 10-mm tubes on a Bruker WP 80 SI instrument. We thank M. Dettlaff for recording the spectra.

Sodium Pentamethylcyclopentadienide (NaC_5Me_5). $NaNH_2$ (50% in toluene) was washed three times with dry pentane and dried in vacuo. A 250-mL Schlenk flask, furnished with a pressure-equalized dropping funnel, was charged with 9.75 g (0.25 mol) of $NaNH_2$ suspended in 50 mL of dry THF. The suspension was cooled to 0 °C. C_5Me_5H (27.2 g, 0.2 mol in 100 mL of dry THF) was added dropwise over a period of 60 min. Gas evolution was observed shortly after the addition was started. After all the C_5Me_5H was added, the reaction mixture was allowed to warm to room temperature and stirred for another 60 min. For removal of NH_3 from the solution, the reaction mixture was concentrated to about 100 mL and THF (100 mL) was added. The suspension then was filtered to remove unreacted $NaNH_2$. The resulting clear solution was cooled to −10 °C, and colorless crystals were obtained. Recrystallization of the crude product from 100 mL of THF at −10 °C yielded pure NaC_5Me_5 in 70% yield relative to C_5Me_5H. NaC_5Me_5 was dissolved in THF to obtain an approximately 1 M solution. The exact concentration was determined by hydrolysis of an exactly determined volume of this solution and subsequent titration with 0.1 N HCl against methyl orange.

Potassium Pentamethylcyclopentadienide (KC_5Me_5). C_5Me_5H (34 g, 0.25 mol) in 50 mL of dme was added to a suspension of 9.75 g (0.25 mol) of chopped K with stirring. The reaction mixture was refluxed for 6 h, and after being left standing for additional 12 h at room temperature, the clear solution was decanted from the precipitated KC_5Me_5, which was washed twice with dry pentane; yield 59.4 g (90%) $KC_5Me_5(dme)$.

Bis(diethyl ether)sodium Bis(pentamethylcyclopentadienyl)dichloropraseodymate(III) (1). $PrCl_3$ (1.6 g, 6.3 mmol) was suspended in 50 mL of dry THF in a 100-mL Schlenk flask equipped with a pressure-equalizing dropping funnel. The magnetically stirred suspension was treated dropwise over 40 min with 12.6 mmol of NaC_5Me_5 (16.6 mL of a 0.76 M solution in THF) at room temperature. During the addition the amount of solid decreased and a cloudy greenish solution was obtained. After all of the NaC_5Me_5 was added, the mixture was stirred for another 4 h at room temperature. Subsequently the THF was stripped in vacuo, and the residue was extracted with three 70-mL portions of dry ether. The combined ether fractions were concentrated to 80 mL and cooled to −10 °C. Greenish crystals of 1 could be collected the next day in 42% yield (1.7 g). The compound decomposed above room temperature, losing ether. Anal. Calcd for $C_{28}H_{50}Cl_2NaPrO_2$: C, 51.46; H, 7.71. Found: C, 51.11; H, 6.81.

From the mother liquor some light green $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Pr(C_5Me_5)_2$ could be collected; decomp pt 250 °C. Anal. Calcd for $C_{40}H_{60}Cl_2Pr_2$: C, 53.75; H, 6.78. Found: C, 53.62; H, 7.43.

Bis(diethyl ether)sodium Bis(pentamethylcyclopentadienyl)dichlorogadolinate(III) (2). This compound was prepared from 4.19 g (15.9 mmol) of $GdCl_3$ in 30 mL of THF and 32 mmol of NaC_5Me_5 (39 mL of a 0.815 M solution in THF) by using the method described for 1. The colorless crystals of 2 decomposed at room temperature during drying in vacuo, losing ether. Anal. Calcd for the ether-free product $C_{20}H_{30}Cl_2GdNa$: C, 46.08; H, 5.80. Found: C, 46.65; H, 6.38.

Bis(diethyl ether)sodium Bis(pentamethylcyclopentadienyl)dichloroterbate(III) (3). This compound was prepared from 2.99 g (11.3 mmol) of $TbCl_3$ in 50 mL of THF and 23 mmol of NaC_5Me_5 (27 mL of a 0.85 M solution in THF) by using the method described for 1. The colorless crystals lose ether above 50 °C. Anal. Calcd for $C_{28}H_{50}Cl_2NaO_2Tb$: C, 50.08; H, 7.50; Cl, 10.56; Tb, 23.66. Found: C, 49.21; H, 7.21; Cl, 9.70; Tb, 24.83.

Bis(diethyl ether)sodium Bis(pentamethylcyclopentadienyl)dichlorodysprosate(III) (4). This compound was prepared from 2.89 g (10.75 mmol) of $DyCl_3$ in 50 mL of THF and 22 mmol of NaC_5Me_5 (28 mL of a 0.786 M solution in THF) by using the method described for 1: yield 3.05 g (42%) of 4. The colorless crystals lose ether above 50 °C. Mass spectrum: *m/e* 469 ($Cp^*{}_2DyCl^+$), 434 ($Cp^*{}_2Dy^+$), 334(Cp^*DyCl^+). Anal. Calcd for $C_{28}H_{50}Cl_2DyO_2$: C, 49.82; H, 7.46. Found: C, 50.76; H, 7.19.

Bis(pentamethylcyclopentadienyl)holmium Chloride–Tetrahydrofuran (5). This compound was prepared from 1.78 g (6.56 mmol) of $HoCl_3$ in 30 mL of THF and 13.1 mmol of NaC_5Me_5 (35.0 mL of a 0.375 M solution in THF) by using the method described for 1. The light brown crystals decompose above 300 °C with evolution of THF. Mass spectrum: *m/e* 470 ($Cp^*{}_2HoCl^+$), 435($Cp^*{}_2Ho^+$), 335(Cp^*HoCl^+). Anal. Calcd for $C_{24}H_{38}ClHoO$: C, 53.09; H, 7.05; Cl, 6.53; Ho, 30.38. Found: C, 52.65; H, 7.13; Cl, 6.48; Ho, 29.89.

Bis(diethyl ether)sodium Bis(pentamethylcyclopentadienyl)dichloroerbate(III) (6). This compound was prepared from 2.00 g (7.31 mmol) of $ErCl_3$ in 30 mL of THF and 15 mmol of NaC_5Me_5 (50 mL of a 0.30 M solution in THF) by using the method described for 1. The pink crystals lose ether above 50 °C. Anal. Calcd for $C_{28}H_{50}Cl_2ErNaO_2$: C, 49.47; H, 7.41. Found: C, 48.86; H, 7.26.

Bis(diethyl ether)sodium Bis(pentamethylcyclopentadienyl)dichlorothulate(III) (7). This compound was prepared from 3.62 g (13.2 mmol) of $TmCl_3$ in 30 mL of THF and 26.3 mmol of NaC_5Me_5 (31 mL of a 0.85 M solution in THF) by using the method described for 1. The green crystals decompose above 50 °C, losing ether. Anal. Calcd for $C_{28}H_{50}Cl_2NaO_2Tm$: C, 49.35; H, 7.39. Found: C, 49.47; H, 7.14.

Bis(diethyl ether)sodium Bis(pentamethylcyclopentadienyl)dichloroytterbate(III) (8). This compound was prepared from 1.57 g (5.62 mmol) of $YbCl_3$ in 30 mL of THF and 11.2 mmol of NaC_5Me_5 (13.2 mL of a 0.85 M solution in THF) by using the method described for 1. After addition of NaC_5Me_5 to the $YbCl_3$ suspension, a blue solution appears which later turned to purple; yield 2.43 g (63%) of purple crystals of 8, which lose

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ether at 190 °C. The ether-free material decomposed at 270 °C. Anal. Calcd for $C_{28}H_{50}Cl_2NaO_2Yb$: C, 49.04; H, 7.36; Cl, 10.34; Na, 3.35; Yb, 25.24. Found: C, 48.77; H, 7.05; Cl, 10.18; Na, 3.34; Yb, 25.55.

Bis(diethyl ether)sodium Bis(pentamethylcyclopentadienyl)dichlorolutetate(III) (9). This compound was prepared from 1.7 g (6.04 mmol) of $LuCl_3$ in 30 mL of THF and 12.1 mmol of NaC_5Me_5 (14.2 mL of a 0.85 M solution in THF) by using the method described for **1**; yield 2.36 g (57%) colorless crystals of **9**, which lose ether at 65 °C. The ether-free material decomposes at 360 °C. Anal. Calcd for $C_{28}H_{50}Cl_2LuNaO_2$: C, 48.91; H, 7.33; Cl, 10.31; Na, 3.34; Lu, 25.45. Found: C, 49.37; H, 7.63; Cl, 10.55; Na, 2.89; Lu, 27.35.

Bis(dimethoxyethane-*O*,*O*′)potassium Bis(pentamethylcyclopentadienyl)dichlorolanthanate(III) (10). Solid KC_5Me_5(dme) (13.2 g, 50 mmol) was added via a Schlenk tube at room temperature to a slurry of 6.1 g (24.9 mmol) of $LaCl_3$ in 150 mL of THF. The mixture was stirred at room temperature for several days until most of the solid material dissolved. Volatile materials were removed in vacuo, and the residue was extracted three times with 50 mL of dme each. After filtration the clear solution was cooled to −20 °C. Colorless crystals were obtained by decanting the solvent and carefully drying in vacuo; yield 2.61 g (15%) of colorless **10**, which lose dme above 60 °C. Anal. Calcd for $C_{28}H_{50}Cl_2KLaO_4$: C, 48.07; H, 7.20. Found: C, 47.52; H, 6.59.

Bis(dimethoxyethane-*O*,*O*′)potassium Bis(pentamethylcyclopentadienyl)dichlorocerate(III) (11). This compound was prepared from 3.77 g (15.3 mmol) of $CeCl_3$ in 100 mL of THF and 8.17 g (30.9 mmol) of KC_5Me_5(dme) by using the method described for **10**. After 5 days of stirring at room temperature and 2 days of refluxing, 1.50 g (14%) of yellow **11** was isolated. Mass spectrum: *m*/*e* 445 ($Cp^*{}_2CeCl^+$), 410 ($Cp^*{}_2Ce^+$), 310 (Cp^*CeCl^+). Anal. Calcd for $C_{28}H_{50}CeCl_2KO_4$: C, 47.99; H, 7.19. Found: C, 50.10; H, 7.05.

Bis(dimethoxyethane-*O*,*O*′)sodium Bis(pentamethylcyclopentadienyl)dichloropraseodymate(III) (12). This compound was prepared like **1** from 2.34 g (9.5 mmol) of $PrCl_3$ and 19.0 mmol of NaC_5Me_5 (25 mL of a 0.76 M solution in THF). Upon the addition of NaC_5Me_5 to the $PrCl_3$ suspension, the reaction mixture turned to green. The crystals are recrystallized from dme; yield 3.1 g (47%) of light green crystals of **12**, which lose dme at 152 °C. Anal. Calcd for $C_{28}H_{50}Cl_2NaO_4Pr$: C, 49.06; H, 7.35; Cl, 10.34; Pr, 20.56. Found: C, 48.53; H, 7.52; Cl, 10.34; Pr, 20.34.

Bis(dimethoxyethane-*O*,*O*′)sodium Bis(pentamethylcyclopentadienyl)dichlorogadolinate(III) (13). This compound was prepared from 3.60 g (13.7 mmol) of $GdCl_3$ in 40 mL of THF and 28 mmol of NaC_5Me_5 (36 mL of a 0.77 M solution in THF) by using the method described for **12**: yield 4.7 g (49%) of colorless crystals of **13**; decomp pt 50 °C. Mass spectrum: *m*/*e* 463 ($Cp^*{}_2GdCl^+$), 428 ($Cp^*{}_2Gd^+$), 328 (Cp^*GdCl^+). Anal. Calcd. for $C_{28}H_{50}Cl_2GdNaO_4$: C, 47.94; H, 7.18. Found: C, 46.76; H, 7.25.

Bis(dimethoxyethane-*O*,*O*′)sodium Bis(pentamethylcyclopentadienyl)dichloroterbate(III) (14). This compound was prepared from 1.28 g (4.76 mmol) of $TbCl_3$ in 40 mL of THF and 10 mmol of NaC_5Me_5 (13 mL of a 0.77 M solution in THF) by using the method described for **12**: yield 2.16 g (64.5%) of colorless crystals of **14**; decomp pt 50 °C. Mass spectrum: *m*/*e* 464 ($Cp^*{}_2TbCl^+$), 428 ($Cp^*{}_2Tb^+$), 329 (Cp^*TbCl^+). Anal. Calcd for $C_{28}H_{50}Cl_2NaO_4Tb$: C, 47.80; H, 7.16; Cl, 10.08; Tb, 22.59. Found: C, 47.22; H, 7.38; Cl, 9.58; Tb, 22.40.

Bis(dimethoxyethane-*O*,*O*′)sodium Bis(pentamethylcyclopentadienyl)dichlorodysprosate(III) (15). This compound was prepared from 2.89 g (10.75 mmol) of $DyCl_3$ in 100 mL of THF and 22 mmol of NaC_5Me_5 (28 mL of a 0.77 M solution in THF) by using the method described for **12**: yield 3.27 g (43%) of colorless crystals of **15**; decomp pt 50 °C. Mass spectrum: *m*/*e* 469 ($Cp^*{}_2DyCl^+$), 434 ($Cp^*{}_2Dy^+$), 334 (Cp^*DyCl^+). Anal. Calcd for $C_{28}H_{50}Cl_2DyNaO_4$: C, 47.56; H, 7.13; Cl, 10.03; Dy, 22.98. Found: C, 47.23; H, 7.54; Cl, 9.56; Dy, 21.57.

Bis(dimethoxyethane-*O*,*O*′)sodium Bis(pentamethylcyclopentadienyl)dichloroholmate(III) (16). This compound was prepared from 2.78 g (10.2 mmol) of $HoCl_3$ in 30 mL of THF and 21 mmol of NaC_5Me_5 (34 mL of a 0.61 M solution in THF) by using the method described for **12**: yield 2.91 g (40%) of brownish crystals of **16**; decomp pt 50 °C. Mass spectrum: *m*/*e* 470 ($Cp^*{}_2HoCl^+$), 435 ($Cp^*{}_2Ho^+$), 335 (Cp^*HoCl^+). Anal. Calcd for $C_{28}H_{50}Cl_2HoNaO_4$: C, 47.40; H, 7.10; Cl, 9.99; Ho, 23.25. Found: C, 45.80; H, 7.15; Cl, 9.34; Ho, 22.37.

Bis(dimethoxyethane-*O*,*O*′)sodium Bis(pentamethylcyclopentadienyl)dichloroerbate(III) (17). This compound was prepared from 2.2 g (8.0 mmol) of $ErCl_3$ in 50 mL THF and 14.6 mmol NaC_5Me_5 (19 mL of a 0.77 M solution in THF) by using the method described for **12**: yield 2.35 g (41.3%) of pink crystals of **17**; decomp pt 50 °C. Mass spectrum: *m*/*e* 473 ($Cp^*{}_2ErCl^+$), 436 ($Cp^*{}_2Er^+$), 338 (Cp^*ErCl^+). Anal. Calcd for $C_{28}H_{50}Cl_2ErNaO_4$: C, 47.25; H, 7.06; Cl, 9.96; Er, 23.49. Found: C, 46.24; H, 7.16; Cl, 10.04; Er, 24.39.

Bis(dimethoxyethane-*O*,*O*′)sodium Bis(pentamethylcyclopentadienyl)dichlorothulate(III) (18). This compound was prepared from 2.73 g (9.92 mmol) of $TmCl_3$ in 50 mL of THF and 20 mmol of NaC_5Me_5 (26 mL of a 0.77 M solution in THF) by using the method described for **12**: yield 5.17 g (73%) of green-yellow crystals of **18**; decomp pt 50 °C. Mass spectrum: *m*/*e* 474 ($Cp^*{}_2TmCl^+$), 438 ($Cp^*{}_2Tm^+$), 339 (Cp^*TmCl^+). Anal. Calcd for $C_{28}H_{50}Cl_2NaO_4Tm$: C, 47.13; H, 7.06; Cl, 9.94; Tm, 23.68. Found: C, 46.42; H, 7.12; Cl, 9.33; Tm, 22.89.

(*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine)lithium Dimethylbis(pentamethylcyclopentadienyl)lanthanate(III) (19). A slurry of 5.49 g (20.8 mmol) of KC_5Me_5(dme) in 50 mL of tetrahydrofuran was added at room temperature to a slurry of 2.56 g (10.4 mmol) of $LaCl_3$ in 50 mL of tetrahydrofuran. The mixture was stirred for 2 days and then cooled to −78 °C. After that, 1.37 mL (10.4 mmol) of tmed and 13.3 mL of a 1.57 M solution of methyllithium in diethyl ether were added within 2 h. The solution was stirred at −78 °C for 1 h and warmed to room temperature. Volatile materials were removed, and the oily residue was diluted in diethyl ether. After filtration the clear solution was cooled to −20 °C overnight. Colorless crystals were obtained the next day by decanting the solvent and carefully drying in vacuo: yield 0.58 g (10%) of **19**; decomp pt 40 °C. Anal. Calcd for $C_{28}H_{52}LaLiN_2$: C, 59.78; H, 9.32; N, 4.98. Found: C, 56.94; H, 9.57; N, 4.83.

(*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine)lithium Dimethylbis(pentamethylcyclopentadienyl)praseodymate(III) (20). This compound was prepared from 1.97 g (7.96 mmol) of $PrCl_3$, 15.9 mmol of NaC_5Me_5 (20.1 mL of a 0.76 M solution in THF), 1 mL (8 mmol) of tmed, and 10.1 mL of an 1.57 M solution of methyllithium in diethyl ether by using the method described for **19**. Greenish crystals of **20** were obtained: yield 1.75 g (39%); decomp pt 125 °C. Anal. Calcd for $C_{28}H_{52}LiN_2Pr$: C, 59.57; H, 9.28; Li, 1.23. Found: C, 58.13; H, 9.86; Li, 1.04.

(*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine)lithium Dimethylbis(pentamethylcyclopentadienyl)lutetate(III) (21). This compound was prepared from 1.36 g (4.83 mmol) of $LuCl_3$, 9.66 mmol of NaC_5Me_5 (14 mL of a 0.70 M solution in THF), 0.75 mL (5.0 mmol) of tmed, and 8.0 mL of an 1.2 M solution of methyllithium in diethyl ether by using the method described for **19**. Colorless crystals of **21** were obtained; yield 1.79 g (62%). Anal. Calcd for $C_{28}H_{52}LiLuN_2$: C, 56.18; H, 8.76; N, 4.68. Found: C, 56.62; H, 9.12; N, 4.83.

Bis(tetrahydrofuran)lithium Dimethylbis(pentamethylcyclopentadienyl)lutetate(III) (22). This compound was prepared from 2.47 g (8.77 mmol) of $LuCl_3$, 17.5 mmol of NaC_5Me_5 (29 mL of a 0.61 M solution in THF), and 11.7 mL of an 1.50 M solution of methyllithium in diethyl ether by using the method described for **19** but without addition of tmed. Colorless crystals of **22** were obtained: yield 3.7 g (68%); decomp pt 45 °C. Anal. Calcd for $C_{30}H_{52}LiLuO_2$: C, 57.50; H, 8.36; Li, 1.11. Found: C, 58.24; H, 8.92; Li, 1.01.

Tris(dimethoxyethane-*O*,*O*′)lithium Bis[(trimethylsilyl)methyl]bis(pentamethylcyclopentadienyl)praseodymate(III) (23). A 3.64-g (5.6-mmol) sample of **1** in 50 mL of tetrahydrofuran was cooled to −78 °C, and a solution of 11.2 mmol of [(trimethylsilyl)methyl]lithium (14.7 mL of a 0.765 M solution in pentane) was added within 2 h. After one additional hour of stirring the reaction mixture was warmed to room temperature; volatile materials were removed, and the residue was extracted with dme. After filtration the clear solution was cooled to −20 °C overnight. The precipitated green crystals were recrystallized twice from dme, yielding 1.69 g (35%) of **23**, which loses the solvent at 62 °C. The dme-free residue decomposes at 108 °C. Anal. Calcd for $C_{40}H_{82}LiO_6PrSi_2$: C, 55.66; H, 9.58; Li, 0.80; Pr, 16.33. Found: C, 55.92; H, 9.72; Li, 0.84; Pr, 16.56.

Tris(dimethoxyethane-*O*,*O*′)lithium Bis[(trimethylsilyl)methyl]bis(pentamethylcyclopentadienyl)lutetate(III) (24). This compound was prepared from 1.74 g (6.20 mmol) of $LuCl_3$, 12.4 mmol of NaC_5Me_5 (16.5 mL of a 0.75 M solution in THF), and 16.2 mL of a 0.765 M solution of [(trimethylsilyl)methyl]lithium in pentane by using the method described for 19 but without adding tmed. The resulting colorless compound was recrystallized from dme, yielding 1.9 g (34%) of colorless 24; decomp pt 98 °C. Anal. Calcd for $C_{40}H_{82}LiLuO_6Si_2$: C, 53.54; H, 9.21; Li, 0.77. Found: C, 53.58; H, 9.58; Li, 0.74.

Crystal Structure of 12. Suitable crystals of 12 were obtained through recrystallization from a dme solution. The crystals were stored under dme. A small amount of this suspension was transferred into a device similar to that reported by Veith and Bärninghausen.[22] An irregular shaped crystal with an approximate diameter of 0.25 mm was selected, glued with grease on top of a glass fiber, and placed in the nitrogen beam of the diffractometer.

Initial investigations revealed the crystal system to be orthorhombic. Cell dimensions were determined by least squares from the $+2\theta$ and -2θ values of 48 strong reflections centered with Mo $K\alpha_1$ radiation ($\lambda = 0.709\,26$ Å) at 138 (2) K. All intensities $0 \rightarrow h$, $0 \rightarrow k$, $0 \rightarrow l$ in the 2θ range $1° \leq 2\theta \leq 44.4°$ were measured at 138 (2) K, applying θ–2θ scans and Mo Kα radiation ($\lambda = 0.710\,69$ Å). Three intensity check reflections were measured every 2 h of X-ray exposure time. The maximum fluctuation for these reflections was 1.7%. Corresponding corrections were applied to the raw intensities. The crystal orientation was checked after each 200 intensity measurements by scanning three orientation check reflections. In case of an angular change greater than 0.1° an array of 20 reflections was recentered and a new orientation matrix was calculated.

The raw data were corrected for Lorentz and polarization effects and converted into structure factors. No absorption correction was made ($\mu = 15.68$ cm^{-1}). From the systematic absent reflections ($h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) the space group was determined to be either $P2_1ca$ (nonstandard setting of $Pca2_1$, no. 29) or $Pmca$ (nonstandard setting of $Pbcm$, no. 57). Inspection of a three-dimensional Patterson map revealed that $P2_1ca$ with two molecules per asymmetric unit is the correct choice. The successful refinement of the structure (no correlation between the two independent molecules per asymmetric unit was observed) confirmed the space group assignment.

The positional parameters for the two praseodymium atoms were calculated from the Patterson map. A difference Fourier map based on the metal atom phases revealed the positions of all other non-hydrogen atoms in the asymmetric unit. The positional parameters of these atoms were refined by full-matrix least squares with anisotropic thermal parameters for Pr, Cl, Na, and O and isotropic ones for all carbon atoms. Hydrogen positions were calculated but not refined for the secondary carbon atoms of the dme molecules (d(C–H) = 0.95 Å)[23] and added to the structure model with a constant isotropic temperature factor ($U_{iso,H} = 0.05$ Å^2). Unit weights were used throughout the refinement. A difference Fourier map based on the final structure model showed no strong peaks (maximum, 0.95 e/Å^3; minimum −1.06 e/Å^3).

All calculations were performed with the use of the program SHELX.[24] Atomic scattering factors for Pr and Na were taken from the tabulations of Cromer and Waber,[25] and anomalous dispersion terms were from Cromer and Liberman[26].

Additional data pertinent to the crystal structure determination are summarized in Table I. Final atomic positional parameters are listed in Table II. The atomic numbering scheme followed in these listings is identified in Figure 5. Selected interatomic distances and angles are listed in Tables III and IV, respectively.

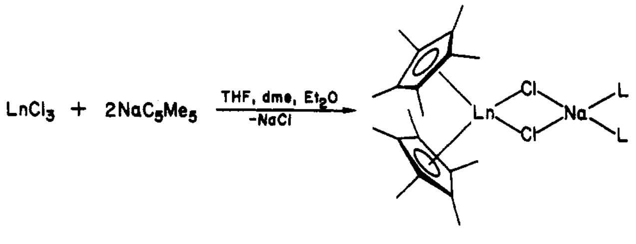
Table I. Crystal and Data Collection Parameters for $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$[a]

formula	$C_{28}H_{50}Cl_2NaO_4Pr$
fw	685.51
space group[b]	$P2_1ca$
a,[c] Å	16.032 (11)
b, Å	16.503 (6)
c, Å	25.084 (9)
V, Å^3	6636.6
Z	8
ρ_{calcd}, g·cm^{-3}	1.372
μ, cm^{-1}	15.68
$F(000)$	2832
diffractometer	Enraf-Nonius CAD-4
radiatn λ, Å	Mo Kα, 0.710 69
temp, K	138 (2)
scan technique	θ–2θ
scan speed	variable, max scan time 60 s
2θ limits, deg	$1 \leq 2\theta \leq 44.4$
no. of collected data	4645
no. of unique data	4345
no. of obsd data	3240 ($I > 3\sigma(I)$)
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0.0476
$R_w = [\sum w \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2 / \sum w \lvert F_o\rvert^2]^{1/2}$	0.0524
no. of parameters	392

[a] Estimated standard deviations of the last significant digit are given in parentheses. [b] Based upon systematic absent reflections: $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$. [c] Final lattice parameters were obtained from a least-squares refinement of the $+2\theta$ and -2θ settings of 48 reflections measured with Mo $K\alpha_1$ radiation ($\lambda = 0.709\,26$ Å).

Results and Discussion

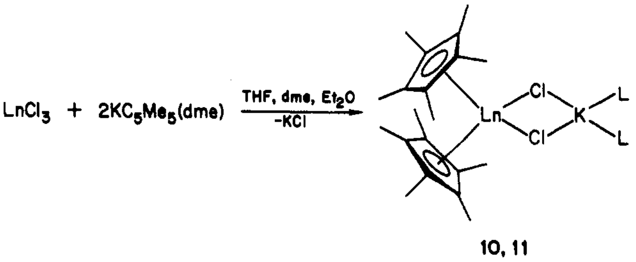
Synthesis of Bis(pentamethylcyclopentadienyl) Halide Derivatives of the Lanthanides. Lanthanide trichlorides $LnCl_3$ react in tetrahydrofuran with pentamethylcyclopentadienylsodium in the molar ratio 1:2 to give the compounds $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Na(L)_2$ with L = diethyl ether (Et_2O) or dimethoxyethane (dme). Attempts to prepare the corresponding lanthanum and cerium complexes in the same manner were unsuccessful. However, by using pentamethylcyclopentadienylpotassium, it was possible to synthesize also the complexes with Ln = La and Ce (eq 1 and 2).



1-9, 12-18

(1)

L = Et$_2$O(1-9), dme(12-18)



10, 11

(2)

Ln = Ce, L = dme(10), Ln = La, L = dme(11)

The sodium chloride complexes can be isolated with diethyl ether (1–9) or dimethoxyethane (12–18) as stabi-

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Table II. Final Positional Parameters for $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$[a]

molecule 1				molecule 2			
atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Pr1	0.50000[b]	−0.00534 (6)	0.33668 (4)	Pr2	0.44655 (7)	0.50006 (7)	0.08103 (3)
Cl1	0.3300 (5)	−0.0058 (4)	0.3417 (2)	Cl3	0.6154 (5)	0.4787 (4)	0.0931 (2)
Cl2	0.5020 (5)	−0.0267 (3)	0.4447 (2)	Cl4	0.4343 (4)	0.5207 (3)	0.1887 (2)
Na1	0.3291 (6)	−0.0227 (5)	0.4537 (3)	Na2	0.6022 (6)	0.4959 (5)	0.2067 (3)
C1	0.4884 (17)	0.1404 (13)	0.2815 (9)	C31	0.4410 (13)	0.3336 (10)	0.0933 (7)
C2	0.4749 (11)	0.1617 (10)	0.3366 (8)	C32	0.4572 (13)	0.3465 (10)	0.0374 (7)
C3	0.5564 (13)	0.1513 (11)	0.3646 (8)	C33	0.3826 (13)	0.3771 (11)	0.0169 (8)
C4	0.6130 (15)	0.1241 (12)	0.3264 (9)	C34	0.3255 (15)	0.3863 (12)	0.0590 (9)
C5	0.5771 (15)	0.1151 (13)	0.2760 (9)	C35	0.3602 (13)	0.3594 (11)	0.1052 (8)
C6	0.4204 (17)	0.1429 (14)	0.2385 (10)	C36	0.5104 (15)	0.2952 (11)	0.1315 (7)
C7	0.3967 (14)	0.1938 (12)	0.3596 (8)	C37	0.5352 (13)	0.3196 (12)	0.0074 (8)
C8	0.5714 (16)	0.1746 (14)	0.4219 (10)	C38	0.3649 (13)	0.3903 (12)	−0.0430 (8)
C9	0.7066 (16)	0.1122 (14)	0.3413 (10)	C39	0.2325 (14)	0.4108 (12)	0.0546 (9)
C10	0.6224 (18)	0.1043 (15)	0.2215 (10)	C40	0.3220 (15)	0.3487 (13)	0.1607 (9)
C11	0.4912 (14)	−0.1720 (11)	0.3331 (8)	C41	0.4624 (16)	0.6178 (13)	0.0033 (10)
C12	0.4673 (15)	−0.1481 (14)	0.2812 (10)	C42	0.5004 (18)	0.6509 (13)	0.0461 (9)
C13	0.5420 (15)	−0.1131 (13)	0.2547 (9)	C43	0.4291 (15)	0.6681 (12)	0.0828 (9)
C14	0.6116 (14)	−0.1165 (12)	0.2915 (9)	C44	0.3562 (14)	0.6399 (13)	0.0643 (10)
C15	0.5814 (13)	−0.1542 (11)	0.3393 (8)	C45	0.3729 (15)	0.6109 (13)	0.0123 (9)
C16	0.4424 (16)	−0.2158 (12)	0.3726 (8)	C46	0.5095 (20)	0.5938 (16)	−0.0488 (11)
C17	0.3845 (16)	−0.1637 (14)	0.2569 (10)	C47	0.5897 (21)	0.6777 (19)	0.0513 (14)
C18	0.5471 (18)	−0.0883 (15)	0.1963 (10)	C48	0.4619 (22)	0.7137 (18)	0.1385 (12)
C19	0.7029 (17)	−0.0958 (15)	0.2771 (10)	C49	0.2672 (26)	0.6508 (23)	0.0874 (15)
C20	0.6368 (14)	−0.1722 (13)	0.3880 (9)	C50	0.3050 (22)	0.5901 (19)	−0.0279 (13)
C21	0.2189 (15)	−0.1882 (14)	0.4011 (9)	C51	0.4927 (19)	0.3653 (16)	0.2884 (11)
O1	0.2714 (10)	−0.1557 (9)	0.4423 (6)	O5	0.5696 (13)	0.3877 (10)	0.2673 (8)
C22	0.2538 (16)	−0.1936 (12)	0.4923 (10)	C52	0.6334 (24)	0.3334 (20)	0.2761 (14)
C23	0.3221 (18)	−0.1762 (16)	0.5313 (11)	C53	0.7173 (33)	0.3581 (30)	0.2591 (23)
O2	0.3273 (11)	−0.0904 (9)	0.5404 (6)	O6	0.7186 (14)	0.4044 (14)	0.2144 (10)
C24	0.3869 (19)	−0.0729 (16)	0.5798 (11)	C54	0.7986 (20)	0.4196 (19)	0.1902 (12)
C25	0.4044 (22)	0.1446 (18)	0.5219 (12)	C55	0.5541 (20)	0.5578 (17)	0.3362 (12)
O3	0.3413 (12)	0.1127 (9)	0.4875 (8)	O7	0.6030 (13)	0.5809 (9)	0.2909 (7)
C26	0.2569 (20)	0.1563 (17)	0.4846 (12)	C56	0.5850 (17)	0.6599 (16)	0.2683 (12)
C27	0.2070 (27)	0.1195 (22)	0.4443 (16)	C57	0.6510 (18)	0.6830 (16)	0.2390 (11)
O4	0.1918 (13)	0.0430 (11)	0.4610 (9)	O8	0.6654 (11)	0.6260 (9)	0.1933 (6)
C28	0.1277 (18)	0.0009 (18)	0.4318 (10)	C58	0.7362 (18)	0.6444 (16)	0.1597 (11)

[a] Estimated standard deviations of the last significant digit are given in parentheses. [b] The *x* axis is a polar axis in $P2_1ca$. *x/a* for Pr1 was fixed to 0.5 to define the origin of the used coordinate system.

lizing base for Na depending on the medium of recrystallization (Table V). Compounds **1**–**9** lose diethyl ether in some cases below room temperature, which turns the crystalline material into a powder. However, crystals of these compounds, obtained below 0 °C and dried very carefully at this temperature in vacuo, show elemental analyses, indicating a $(C_5Me_5)_2LuCl_2Na(Et_2O)_2$ formula. Due to the facile loss of diethyl ether from some of the crystalline derivatives, it was not possible to determine the exact yield of the reactions leading to **2**, **3**, **5**, **6**, and **7**. Also, the elemental analyses for this derivatives are not satisfactory for all elements.

The powders resulting from loss of diethyl ether at room temperature are not completely ether-free. These materials are then stable up to about 200 °C. They show decomposition points above 200 °C as cited for the stoichiometrical $(C_5Me_5)_2NdCl_2Na(Et_2O)_2$ or the corresponding samarium or ytterbium complexes.[4] Isolation of $(C_5Me_5)_2HoCl_2Na(Et_2O)_2$ was not possible. The isolated compound **5** is sodium-free. Microanalytical data and an X-ray structural analysis[27] indicate a tetrahydrofuran complex of bis(pentamethylcyclopentadienyl)holmium chloride, $(C_5Me_5)_2HoCl(THF)$.

The dme complexes **10**–**18** are much more stable toward loss of solvent. Most of these compounds lose dme around 50 °C. Compound **12** decomposes at 152 °C to the dinuclear, dme-free chlorine-bridged complex $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Pr(C_5Me_5)_2$, which can be isolated from the mother liquor during recrystallization of the diethyl ether complex **1**.

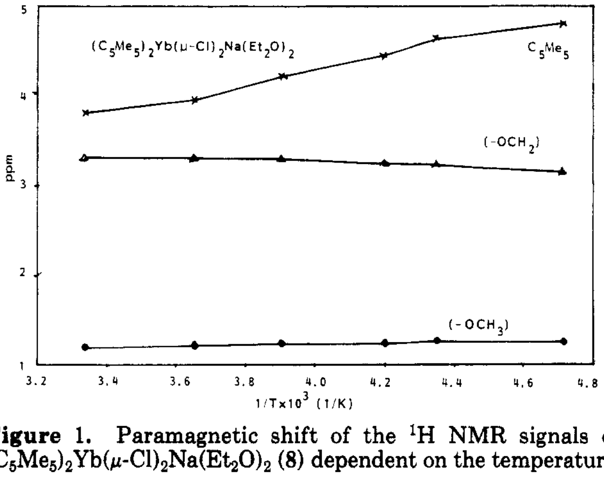

Figure 1. Paramagnetic shift of the ^1H NMR signals of $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Na(Et_2O)_2$ (**8**) dependent on the temperature.

The potassium complexes **10** and **11** are obtained only in very low yields. The cerium compound **11** is extremely sensitive toward moisture and air. It decomposes slowly at room temperature. The isolation of the pure crystalline material is very difficult.

Synthesis of Bis(pentamethylcyclopentadienyl) Alkyl Derivatives of the Lanthanides. $LaCl_3$, $PrCl_3$, and $LuCl_3$ react in tetrahydrofuran with (pentamethylcyclopentadienyl)sodium or -potassium and methyllithium in the presence of tetramethylethylenediamine (tmed) at −78 °C with formation of bis(pentamethylcyclo-

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(27) van der Helm, D.; Loebel, J.; Schumann, H., to be submitted for publication.

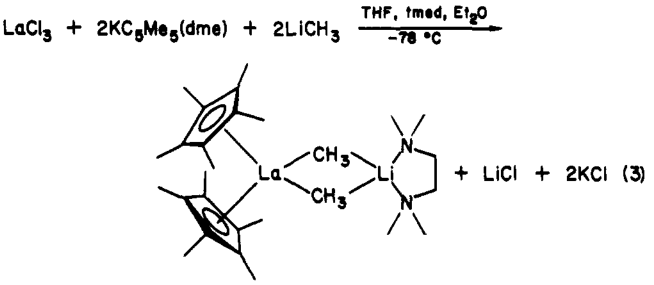
Table III. Selected Interatomic Distances (Å) for $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$[a]

molecule 1		molecule 2	
Pr1⋯Na1[b]	4.025 (9)	Pr2⋯Na2[b]	4.021 (8)
Pr1–Cl1	2.728 (8)	Pr2–Cl3	2.747 (8)
Pr1–Cl2	2.732 (5)	Pr2–Cl4	2.728 (5)
Cl1⋯Cl2[b]	3.793 (9)	Cl3⋯Cl4[b]	3.829 (9)
Pr1–C1	2.78 (2)	Pr2–C31	2.77 (2)
Pr1–C2	2.79 (2)	Pr2–C32	2.77 (2)
Pr1–C3	2.83 (2)	Pr2–C33	2.78 (2)
Pr1–C4	2.81 (2)	Pr2–C34	2.76 (2)
Pr1–C5	2.79 (2)	Pr2–C35	2.77 (2)
Pr1–C11	2.76 (2)	Pr2–C41	2.76 (2)
Pr1–C12	2.79 (2)	Pr2–C42	2.78 (2)
Pr1–C13	2.80 (2)	Pr2–C43	2.79 (2)
Pr1–C14	2.80 (2)	Pr2–C44	2.76 (2)
Pr1–C15	2.78 (2)	Pr2–C45	2.78 (2)
Pr1–Cp1[c]	2.52 (2)	Pr2–Cp3[c]	2.50 (2)
Pr1–Cp2[c]	2.50 (2)	Pr2–Cp4[c]	2.50 (2)
Na1–Cl1	2.822 (10)	Na2–Cl3	2.872 (9)
Na1–Cl2	2.781 (12)	Na2–Cl4	2.760 (11)
Na1–O1	2.40 (2)	Na2–O5	2.40 (2)
Na1–O2	2.45 (2)	Na2–O6	2.41 (2)
Na1–O3	2.40 (2)	Na2–O7	2.54 (2)
Na1–O4	2.46 (2)	Na2–O8	2.40 (2)

molecule 1		molecule 2	
	C–C in the Cyclopentadienyl Groups		
range	1.39 (3)–1.49 (3)	range	1.34 (3)–1.50 (4)
mean	1.45 (4)	mean	1.41 (5)
	$C\text{–}CH_3$ in the Cyclopentadienyl Groups		
range	1.45 (3)–1.56 (3)	range	1.50 (4)–1.67 (4)
mean	1.52 (4)	mean	1.56 (5)
	O–C in the dme Molecules		
range	1.35 (4)–1.53 (4)	range	1.36 (6)–1.50 (3)
mean	1.43 (5)	mean	1.43 (5)
	C–C in the dme Molecules (for Both Molecules)		
range	1.34 (4)–1.50 (4)		

[a] Estimated standard deviations for the last significant digit are given in parentheses. [b] Nonbonded distances. [c] Cp denotes the centroids of the cyclopentadienyl groups (C1–C5, Cp1; C11–C15, Cp2; C31–C35, Cp3; C41–C45, Cp4).

pentadienyl)lanthanide dimethyllithium complexes, which are stabilized by tmed (eq 3 and 4).



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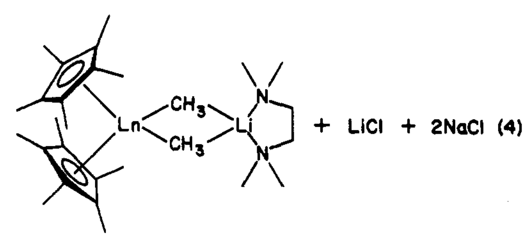


20, Ln=Pr
21, Ln=Lu

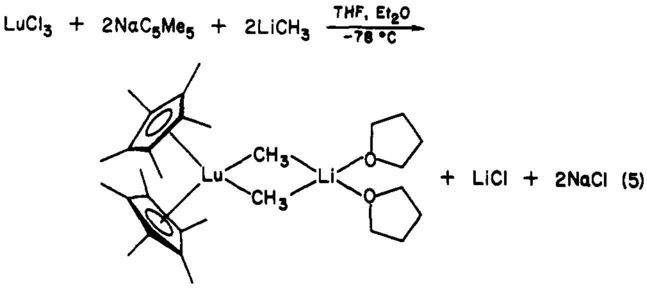
Table IV. Selected Interatomic Angles (deg) for $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$[a]

molecule 1		molecule 2	
Cp1–Pr1–Cp2[b]	134.9 (7)	Cp3–Pr2–Cp4	135.5 (7)
Cp1–Pr1–Cl1	106.2 (5)	Cp3–Pr2–Cl3	103.8 (5)
Cp1–Pr1–Cl2	108.3 (5)	Cp3–Pr2–Cl4	106.0 (4)
Cp2–Pr1–Cl1	105.2 (5)	Cp4–Pr2–Cl3	107.5 (6)
Cp2–Pr1–Cl2	104.3 (5)	Cp4–Pr2–Cl4	105.5 (5)
Cl1–Pr1–Cl2	88.0 (2)	Cl3–Pr2—Cl4	88.7 (2)
Pr1–Cl1–Na1	93.0 (3)	Pr2–Cl3–Na2	91.4 (3)
Pr1–Cl2–Na1	93.8 (3)	Pr2–Cl4–Na2	94.2 (2)
Cl1–Na1–Cl2	85.2 (3)	Cl3–Na2–Cl4	85.6 (3)
Cl1–Na1–O1	88.5 (5)	Cl3–Na2–O5	124.8 (6)
Cl1–Na1–O2	158.5 (5)	Cl3–Na2–O6	87.8 (7)
Cl1–Na1–O3	105.1 (6)	Cl3–Na2–O7	151.7 (5)
Cl1–Na1–O4	92.0 (6)	Cl3–Na2–O8	85.3 (5)
Cl2–Na1–O1	110.7 (5)	Cl4–Na2–O5	90.1 (6)
Cl2–Na1–O2	94.2 (5)	Cl4–Na2–O6	149.5 (7)
Cl2–Na1–O3	88.3 (5)	Cl4–Na2–O7	93.4 (6)
Cl2–Na2–O4	155.2 (6)	Cl4–Na2–O8	104.8 (5)
O1–Na1–O2	71.6 (6)	O5–Na2–O6	69.6 (8)
O1–Na1–O3	157.8 (7)	O5–Na2–O7	83.4 (6)
O1–Na1–O4	93.8 (6)	O5–Na2–O8	147.8 (7)
O2–Na1–O3	96.4 (7)	O6–Na2–O7	106.0 (8)
O2–Na1–O4	97.1 (7)	O6–Na2–O8	104.2 (8)
O3–Na1–O4	68.7 (7)	O7–Na2–O8	67.6 (6)

molecule 1	molecule 2
Range of C–C–C in the Cyclopentadienyl Groups	
106 (2)–113 (2)	103 (2)–113 (2)
Range of $C\text{–}C\text{–}CH_3$ in the Cyclopentadienyl Groups	
120 (2)–129 (2)	111 (2)–136 (2)

[a] Estimated standard deviations of the last significant digit are given in parentheses. [b] See footnote c in Table III.

$LuCl_3$ reacts with NaC_5Me_5 and CH_3Li under the same conditions but without tmed with formation of a methyl-bridged lithium dimethylbis(pentamethylcyclopentadienyl)-lutetium complex, but coordinated with two molecules of tetrahydrofuran at the lithium atom (eq 5).



22

Complexes 19, 20, and 21 are stable at room temperature. In 22 elemental analyses as well as NMR spectra favor the presence of only two coordinated THF molecules, in contrast to the earlier mentioned $(C_5Me_5)_2Lu(CH_3)_2Li(THF)_3$.[28]

The reaction of $PrCl_3$ with NaC_5Me_5 and $LiCH_2SiMe_3$ in the molar ratio 1:2:1 in THF did not yield a pure product. But using pure 1 as the starting material, instead of making a "one-pot reaction", it was possible to prepare the (trimethylsilyl)methyl-substituted praseodymium complex 23 in resonable yield and purity as well as the corresponding lutetium compound 24, which can also been made by a simple "one-pot reaction" from $LuCl_3$, NaC_5Me_5, and $LiCH_2SiMe_3$ in the presence of dme (eq 6).

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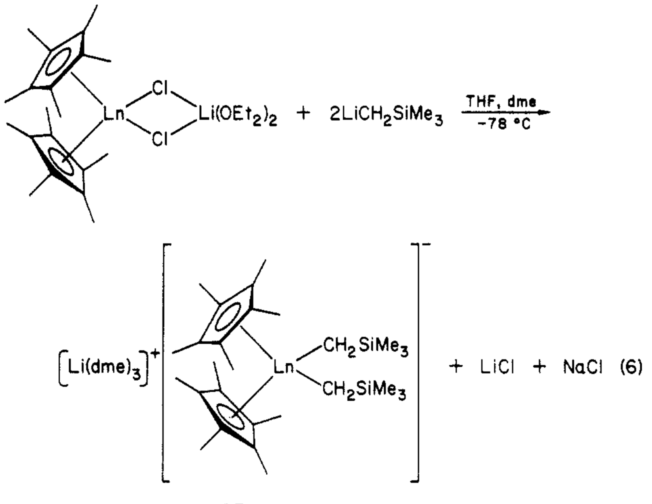
(28) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337.



(6)

23, Ln=Pr
24, Ln=Lu

Both solid compounds decompose at about 100 °C, **23** in solution at 40 °C with formation of tetramethylsilane. A metallacycle, analogous to that found in the decomposition of the neutral thorium complex $(C_5Me_5)_2Th(CH_2SiMe_3)_2$,[29] could not be identified in the remaining decomposition products.

23 and **24** are cation–anion pairs with terminal Me_3SiCH_2– groups bound to praseodymium or lutetium, respectively. The NMR spectra of both compounds prove the presence of three dme ligands and therefore this prediction. The same cation–anion pair could be found in $[Li(dme)_3][(C_5H_5)_2Sm(SiMe_3)_2]$.[30] The bulky (trimethylsilyl)methyl groups prevent bridging to the lithium atom.

NMR Spectroscopy. The ^1H NMR and ^{13}C NMR data of the diamagnetic lanthanum and lutetium complexes as well as some data of the paramagnetic complexes **1**, **8**, **12**, **20**, and **23** are given in Tables VI and VII. The diamagnetic derivatives **9**, **10**, **19**, **21**, **22**, and **24** show in THF-d_8 the expected ^1H and ^{13}C signals for the pentamethylcyclopentadienyl groups, the alkyl groups, and the Et_2O, dme, tmed, and THF ligands.

The spectra of the paramagnetic compounds of the lanthanides Pr and Yb show broadened signals, which are temperature dependent. Tables VI and VII show the data at room temperature. Figures 1–4 give the dependence of the paramagnetic shifts of the ^1H NMR signals of **8**, **12**, **20**, and **23**, respectively from the reciprocal absolute temperature, which is linear following the Curie–Weiss law.

Molecular Structure of $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$ (12). Structural data for organometallic compounds of the lighter lanthanides Ce to Nd are rare compared with the data available for the heavier lanthanides Sm to Lu. Praseodymium has the second largest ionic radius in the series of the lanthanides ($r_{Pr}{}^{VIII}$ = 1.126 Å[31]), and its organometallic derivatives are only stable in high coordination numbers such as $[(C_5H_5)_3Pr]_\infty$, coordination number 10,[32] and $(C_5H_5)_3PrCNC_6H_{11}$, coordination number 10,[33] or when stabilized by very bulky ligands like in $[\{C_5H_3(SiMe_3)_2\}_2PrCl]_2$, coordination number 8.[34]

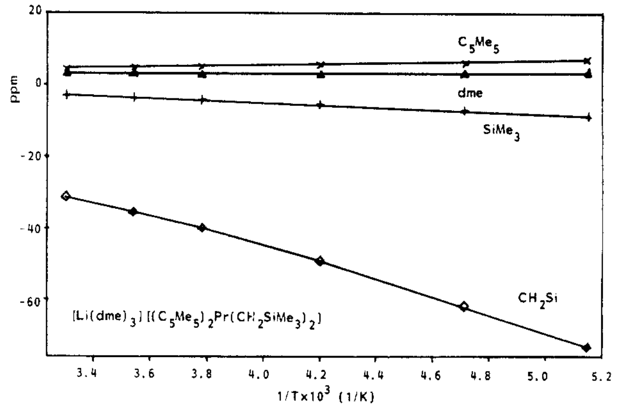


Figure 2. Paramagnetic shift of the ^1H NMR signals of $[Li(dme)_3][(C_5Me_5)_2Pr(CH_2SiMe_3)_2]$ (**23**) dependent on the temperature.

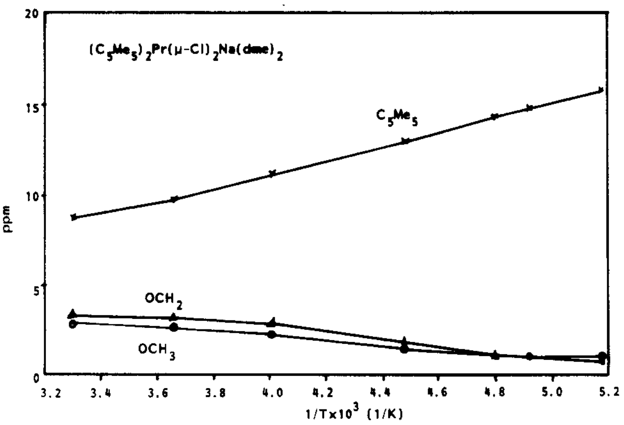


Figure 3. Paramagnetic shift of the ^1H NMR signals of $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$ (**12**) dependent on the temperature.

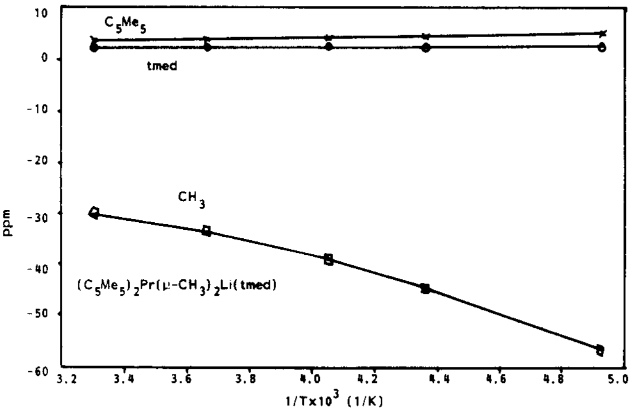


Figure 4. Paramagnetic shift of the ^1H NMR signals of $(C_5Me_5)_2Pr(\mu\text{-}CH_3)_2Li(tmed)$ (**20**) dependent on the temperature.

Compound **12** is the first crystallographically characterized sodium chloride adduct of a bis(pentamethylcyclopentadienyl)lanthanide chloride and the first bis(pentamethylcyclopentadienyl)praseodymium derivative, showing that lighter lanthanides also form stable compounds with this ligand.

The crystal structure of **12** consists of discrete molecules without short contacts. Although there are two crystallographically independent molecules in the asymmetric unit (Figure 5), they do not differ significantly in any respect. Both molecules are comprised of a praseodymium atom residing in the center of a distorted tetrahedron

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[29] Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Organomet. Chem.* **1983**, *250*, 237.

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[34] Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 1190.

Table V. Yields, Colors, and Decomposition Points for Compounds $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2M(L)_2$

Ln	M	L		yield, %	color	decomp pt, °C
Pr	Na	Et_2O	**1**	42	greenish	30
Gd	Na	Et_2O	**2**		colorless	30
Tb	Na	Et_2O	**3**		colorless	50
Dy	Na	Et_2O	**4**	42	colorless	50
Er	Na	Et_2O	**6**		pink	50
Tm	Na	Et_2O	**7**		green	50
Yb	Na	Et_2O	**8**	63	purple	190
Lu	Na	Et_2O	**9**	57	colorless	65
La	K	dme	**10**	15	colorless	60
Ce	K	dme	**11**	14	yellow	30
Pr	Na	dme	**12**	47	light green	152
Gd	Na	dme	**13**	49	colorless	50
Tb	Na	dme	**14**	64.5	colorless	50
Dy	Na	dme	**15**	43	colorless	50
Ho	Na	dme	**16**	40	brownish	50
Er	Na	dme	**17**	41.3	pink	50
Tm	Na	dme	**18**	73	green-yellow	50

Table VI. ^1H NMR Spectral Data for Bis(pentamethylcyclopentadienyl) Halide and Alkyl Derivatives of the Lanthanides[a] in THF-d_8 at 30 °C ($Cp^* = C_5Me_5$)

compd		$\delta(Cp^*)$	$\delta(H_\alpha)$	$\delta(H_\gamma)$	$\delta(Et_2O/dme/tmed/THF)$
$Cp^*{}_2Pr(\mu\text{-}Cl)_2Na(Et_2O)_2$	**1**	9.50			
$Cp^*{}_2Yb(\mu\text{-}Cl)_2Na(Et_2O)_2$	**8**	3.65			1.19 (tr), 3.32 (q)
$Cp^*{}_2Lu(\mu\text{-}Cl)_2Na(Et_2O)_2$	**9**	1.98 (s)			1.19 (tr), 3.48 (q)
$Cp^*{}_2La(\mu\text{-}Cl)_2K(dme)_2$	**10**	1.95 (s)			3.27, 3.42
$Cp^*{}_2Pr(\mu\text{-}Cl)_2Na(dme)_2$	**12**	8.70			2.82, 3.27
$Cp^*{}_2La(\mu\text{-}CH_3)_2Li(tmed)$	**19**	1.97 (s)	−1.43 (s)		2.25 (s), 2.40 (s)
$Cp^*{}_2Pr(\mu\text{-}CH_3)_2Li(tmed)$	**20**	3.55	−30.3		2.16, 2.31
$Cp^*{}_2Lu(\mu\text{-}CH_3)_2Li(tmed)$	**21**	1.93 (s)	−1.77 (s)		2.28 (s), 2.44 (s)
$Cp^*{}_2Lu(\mu\text{-}CH_3)_2Li(THF)_2$	**22**	1.88 (s)	−1.73 (s)		1.83 (m), 3.68 (m)
$[Li(dme)_3][Cp^*{}_2Pr(CH_2SiMe_3)_2]$	**23**	4.47	−31.6	−2.99	3.23, 3.46
$[Li(dme)_3][Cp^*{}_2Lu(CH_2SiMe_3)_2]$	**24**	1.88 (s)	−1.86 (s)	−0.11 (s)	3.26 (s), 3.42 (s)

[a] Chemical shifts are reported in ppm from $Si(CH_3)_4$: s, singlet; tr, triplet; q, quartet; m, multiplet.

Table VII. ^{13}C NMR Spectral Data for Bis(pentamethylcyclopentadienyl) Halide and Alkyl Derivatives of the Lanthanides[a] in THF-d_8 at 30 °C ($Cp^* = C_5Me_5$)

compd		$\delta(C_5(\mathit{CH}_3)_5)$	$\delta(\mathit{C}_5(CH_3)_5)$	$\delta(C_\alpha)$	$\delta(C_\gamma)$	$\delta(Et_2O/dme/tmed/THF)$
$Cp^*{}_2Pr(\mu\text{-}Cl)_2Na(Et_2O)_2$	**1**	12.86				17.2, 61.6
$Cp^*{}_2Yb(\mu\text{-}Cl)_2Na(Et_2O)_2$	**8**	−20.2, −23.1	−156.9, −169.5			
$Cp^*{}_2Lu(\mu\text{-}Cl)_2Na(Et_2O)_2$	**9**	11.88	116.63			15.41, 65.81
$Cp^*{}_2La(\mu\text{-}Cl)_2K(dme)_2$	**10**	11.30	118.63			58.80, 72.70
$Cp^*{}_2Pr(\mu\text{-}Cl)_2Na(dme)_2$	**12**	11.7				58.80, 72.70
$Cp^*{}_2La(\mu\text{-}CH_3)_2Li(tmed)$	**19**	11.11	115.91	25.83		45.88, 58.26
$Cp^*{}_2Pr(\mu\text{-}CH_3)_2Li(tmed)$	**20**	−3.09	231.00			45.99, 58.33
$Cp^*{}_2Lu(\mu\text{-}CH_3)_2Li(tmed)$	**21**	12.10	111.20	22.20		46.00, 58.80
$Cp^*{}_2Lu(\mu\text{-}CH_3)_2Li(THF)_2$	**22**	12.07	111.10	22.20		68.25, 15.62
$[Li(dme)_3][Cp^*{}_2Pr(CH_2SiMe_3)_2]$	**23**	−5.97	180.55		20.23	58.94, 71.84
	23[b]	−9.98	211.40		23.2	58.93, 72.68
$[Li(dme)_3][Cp^*{}_2Lu(CH_2SiMe_3)_2]$	**24**	12.76	112.39	25.87	6.27	58.79, 72.55

[a] Chemical shifts are reported in ppm from $Si(CH_3)_4$. [b] At −26 °C.

formed by the centroids of the five-membered rings and the two μ_2-chlorine atoms. The sodium atoms sit in the center of a distorted octahedron made up by two chlorine atoms and four oxygen atoms of the two dme molecules. Thus the coordination numbers for Pr and Na are 8 and 6, respectively. If **12** is recrystallized from diethyl ether to yield **1**, tetracoordination is observed for Na with only two molecules of Et_2O coordinating to the sodium atom, as indicated by elemental analyses. The tmed-stabilized sodium chloride adducts of bis(pentamethylcyclopentadienyl)ytterbium and samarium chloride are also reported to crystallize with only one molecule of the bidentate base tmed, thus having coordination number 4 for the sodium atom.[4]

This average for the 20 Pr–C(η^5) distances in **12**, 2.78 (2) Å, compares well with this value for $[\{C_5H_3(SiMe_3)_2\}_2PrCl]_2$, 2.76 Å,[34] the only other crystallographically characterized bis(cyclopentadienyl)praseodymium derivative. However, the Pr–Cl distances in **12** (2.728 (8) and 2.732 (5) Å) are significantly shorter than this distance in the homometallic complex mentioned above (2.81 Å[34]). Similar behavior has been observed for ytterbium complexes with a $Yb(\mu\text{-}Cl)_2Yb$ unit (d(Yb–Cl) = 2.628 (2) and 2.647 (2) Å[35]) or a $Yb(\mu\text{-}Cl)_2Li$ unit (d(Yb–Cl) = 2.596 (1) and 2.594 (1) Å[6]). The homometallic complexes have longer Ln–Cl(br) distances since the halide bridges two equally strong Lewis acids in these derivatives, whereas in the alkali-metal halide adducts the halogen atom bridges a trivalent and a monovalent Lewis acid with the stronger interaction being observed for the Ln–halogen bond.

The geometry of the $Ln(\mu\text{-}Cl)_2M$ unit is also different for M = lanthanide and M = alkali metal. In the dilanthanide complexes two large Cp_2Ln units are to be

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(35) Baker, E. C.; Brown, L. D.; Raymond, C. N. *Inorg. Chem.* **1975**, *14*, 1376.

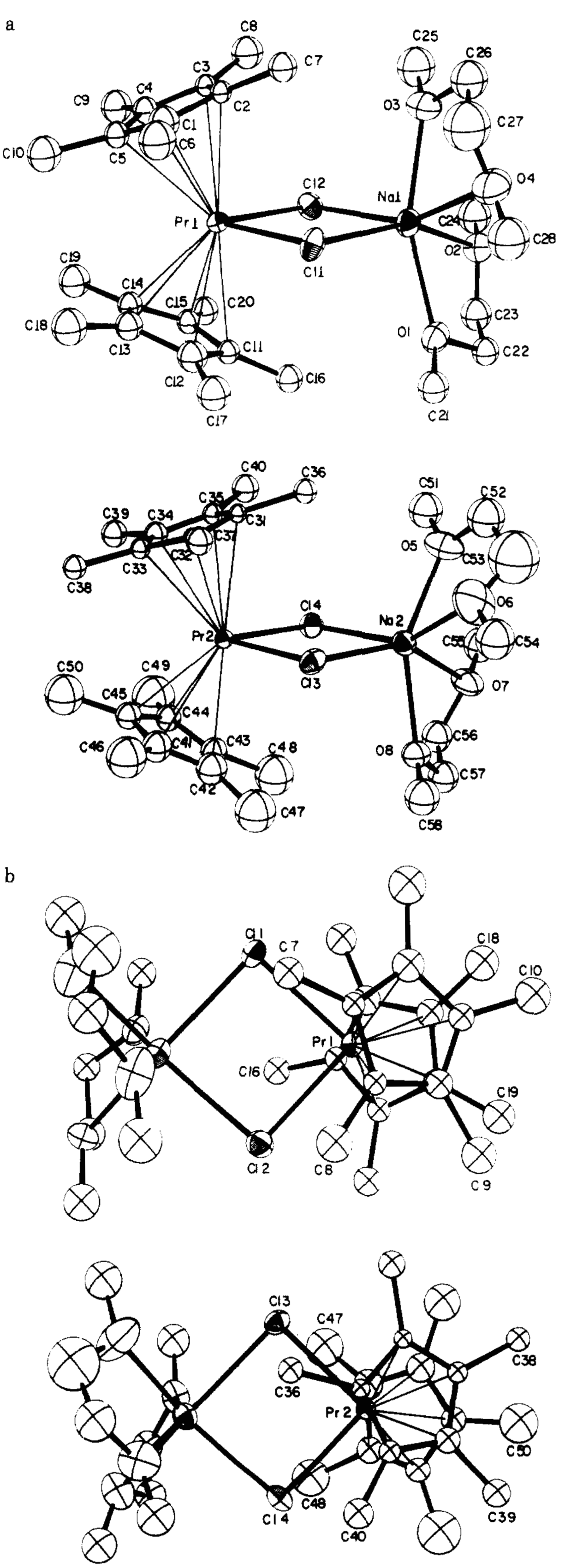

Figure 5. (a) Ortep drawing of the two independent molecules of 12 with the employed numbering scheme. (b) View perpendicular to the Pr(μ-Cl)$_2$Na planes.

bridged, requiring a large Ln–Ln separation. This separation is achived by means of large Ln–Cl–Ln angles and small Cl–Ln–Cl angels. However, the distance between the bridging ligands cannot be much smaller than their contact distance, putting limits on the amount of the expansion of the Ln–Cl–Ln angle and the reduction of the Cl–Ln–Cl angle. Due to these requirements and the relative small size of Y, (C$_5$Me$_5$)$_2$YCl does not crystallize as a symmetrically bridged dimer but instead as (C$_5$Me$_5$)$_2$Y(μ-Cl)YCl(C$_5$Me$_5$)$_2$.[36] For the lanthanides a number of symmetrically bridged Cp$_2$Ln(μ-Cl)$_2$LnCp$_2$ units are observed, with Ln–Cl–Ln angles of 97.95 (5)° (Ln = Yb[35]) and 102° (Ln = Pr[34]) and Cl–Ln–Cl angles of 82.05 (5)° (Ln = Yb[35]) and 78° (Ln = Pr[34]).

In 12 as well as in (C$_5$Me$_5$)$_2$Yb(μ-Cl)$_2$Li(Et$_2$O)$_2$[6] the coordination polyhedron around the alkali metal is much smaller than a Cp$_2$Ln unit, allowing for a shorter Pr–Na or Yb–Li separation than the Ln–Ln distance in the corresponding homometallic derivatives. This provides almost square Ln(μ-Cl)$_2$M units with all four angles closer to 90°. As a result of this geometry the bridging ligands in the alkali-metal halide adducts are stronger more exposed to the action of bridge cleaving ligands, resulting in a greater reactivity of the alkali-metal halide adducts relative to the homometallic complexes. A good example for this enhanced reactivity is also found recently with the bis(cyclopentadienyl)lanthanide methyl derivatives.[37-39] (C$_5$Me$_5$)$_2$Lu(μ-CH$_3$)$_2$Lu(C$_5$Me$_5$)$_2$ is fairly unreactive, whereas (C$_5$Me$_5$)$_2$Lu(μ-CH$_3$)$_2$Li(THF)$_2$ reacts at −78 °C with *tert*-butylmercaptan (t-C$_4$H$_9$SH) to form (C$_5$Me$_5$)$_2$Lu(μ-S-t-C$_4$H$_9$)$_2$Li(THF)$_2$.[40]

Acknowledgment. We thank the Fonds der Chemischen Industrie for a "Doktoranden-Stipendium" (E.H.) as well as for generous support of this work, which was also supported by the Deutsche Forschungsgemeinschaft and by special grants of the TU Berlin within the exchange program TU Berlin/University of Oklahoma and the research projects "Flüssigkristalline Phasen und ihre elektrooptischen Anwendungen" and "Materialien für neue Technologien".

Registry No. **1**, 101932-97-2; **2**, 101932-99-4; **3**, 101933-01-1; **4**, 101933-03-3; **5**, 101933-04-4; **6**, 101933-06-6; **7**, 101933-08-8; **8**, 78128-21-9; **9**, 101933-09-9; **10**, 101933-10-2; **11**, 101933-12-4; **12**, 101933-14-6; **13**, 101933-15-7; **14**, 101933-16-8; **15**, 101933-17-9; **16**, 101933-19-1; **17**, 101933-20-4; **18**, 101933-21-5; **19**, 95029-68-8; **20**, 101933-24-8; **21**, 95029-69-9; **22**, 98858-50-5; **23**, 101933-26-0; **24**, 101953-16-6; NaC$_5$Me$_5$, 40585-51-1; KC$_5$Me$_5$, 94348-92-2; NaNH$_2$, 7782-92-5; C$_5$Me$_5$H, 41539-64-4; PrCl$_3$, 10361-79-2; GdCl$_3$, 10138-52-0; TbCl$_3$, 10042-88-3; DyCl$_3$, 10025-74-8; HoCl$_3$, 10138-62-2; ErCl$_3$, 10138-41-7; TmCl$_3$, 13537-18-3; YbCl$_3$, 10361-91-8; LuCl$_3$, 10099-66-8; LaCl$_3$, 10099-58-8; CeCl$_3$, 7790-86-5; [(trimethylsilyl)methyl]lithium, 1822-00-0.

Supplementary Material Available: Tables of thermal parameters, hydrogen parameters, and selected least-squares planes and a list of observed and calculated structure factors for 12 (20 pages). Ordering information is given on any current masthead page.

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(41) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)