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Registry No. RuO_2, 12036-10-1; $Ru(acac)_3$, 14284-93-6; $Ru_3(CO)_{12}$, 15243-33-1; $Ti(acac)_2(OBu)_2$, 16902-59-3; $Ti(OMe)_4$, 992-92-7; $H_2ZrO_2(OAc)_2$, 14311-93-4; $Co(acac)_3$, 21679-46-9; CO, 630-08-0; $Co_2(CO)_8$, 10210-68-1; $Re_2(CO)_{10}$, 14285-68-8; $MnCO_3$, 598-62-9; Bu_4PI, 3115-66-0; $C_7H_{15}Ph_3PBr$, 13423-48-8; PrOH, 71-23-8; MeOAc, 79-20-9; EtOAc, 141-78-6; PrOAc, 109-60-4; MeOH, 67-56-1; Bu_4PBr, 3115-68-2; AcOH, 64-19-7; EtOH, 64-17-5.

Organometallic Compounds of the Lanthanides. 17.[1] Tris[(tetramethylethylenediamine)lithium] Hexamethyl Derivatives of the Rare Earths

Herbert Schumann,* Jochen Müller, Norbert Bruncks, Harald Lauke, and Joachim Pickardt

Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D-1000 Berlin 12, Bundesrepublik Deutschland

H. Schwarz and Klaus Eckart

Institut für Organische Chemie, Technische Universität Berlin, D-1000 Berlin 12, Bundesrepublik Deutschland

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The trichlorides of yttrium, lanthanum, and the lanthanides react with methyllithium in diethyl ether in the presence of tetramethylethylenediamine (tmed) to give the complexes $[Li(tmed)]_3[Ln(CH_3)_6]$ with Ln = Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. From the reaction of lutetium tri-*tert*-butoxide, tmed, and *tert*-butyllithium in pentane, $[Li(tmed)_2][Lu(t\text{-}C_4H_9)_4]$ has been obtained. The new compounds have been characterized by elemental analyses and IR and NMR spectra. The structure of $[Li(tmed)]_3[Ho(CH_3)_6]$ has been elucidated through complete X-ray analysis. The crystals are rhombohedral with $a = 1280.7\ (20)$ pm, $\alpha = 79.84\ (13)°$, space group $R\bar{3}c$, $Z = 2$, $D(\text{calcd}) = 0.96$ g cm^{-3}, $R = 0.050$, and 1535 observed reflections. The potential of methylating α,β-unsaturated aldehydes and ketones has been explored for $[Li(tmed)]_3[Pr(CH_3)_6]$ and $[Li(tmed)]_3[Sm(CH_3)_6]$, and it was found that 1,2 methylation is favored over 1,4 addition.

Introduction

The first description of an organometallic compound of a rare-earth element, the synthesis of $Sc(C_2H_5)_3$ and $Y(C_2H_5)_3$ in 1938, was an error,[2] and the first attempts to prepare phenyl derivatives of lanthanum and some lanthanides by Gilman and co-workers failed. Biphenyl was the only reaction product isolated from the reactions of $LaCl_3$ with LiC_6H_5 in ether or from La with diphenylmercury at elevated temperatures in a sealed tube.[3] Wilkinson and Birmingham prepared the first organometallic compounds of the rare earths, the tricyclopentadienyl complexes of Sc, Y, La, Ce, Pr, Nd, Sm, and Gd.[4] Fourteen more years were required to demonstrate the synthesis of $Sc(C_6H_5)_3$, the first "homoleptic" η^1-bonded organometallic compound of a rare-earth element.[5] The reaction of phenyllithium with $LaCl_3$ or the trichlorides of some lanthanides did not give analogous derivatives. In the cases of $LaCl_3$ and $PrCl_3$, compounds of the type $Li[Ln(C_6H_5)_4]$ were formed.[6]

A considerable stabilization of "homoleptic" organometallic compounds of the rare earths could be achieved by use of bulky alkyl or aryl groups, such as *tert*-butyl,[7] 2,6-dimethylphenyl,[8] neopentyl,[9] $CH_2Si(CH_3)_3$,[9–11] or $CH[Si(CH_3)_3]_2$,[10] or alkyl and aryl ligands containing built-in chelating groups, like (dimethylamino)-*o*-benzyl or (dimethylamino)methylphenyl.[12,13]

We have found that permethylated complexes of the rare earths can be synthesized by using tetramethylethylenediamine (tmed) as a stabilizing base.[14] We have undertaken single-crystal X-ray diffraction studies of two of these derivatives.[15] Infrared and ^1H and ^{13}C NMR spectra of the compounds have been recorded, and some interesting features are presented.

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 distillation under argon prior to use. Anhydrous rare-earth chlorides were prepared from the pure

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oxides (Auer-Remy, Hamburg, West Germany) by reaction with NH_4Cl.[16] Tetramethylethylenediamine (tmed) was dried and freed of oxygen by refluxing over KOH and distillation under argon. Melting points were determined in sealed, argon-filled capillaries. Elemental analyses were performed by 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. Metal analyses were carried out by complexometric titration against dithizone.[17]

Infrared spectra were recorded as paraffin mulls between CsI plates, using a Perkin-Elmer 580 B (200–4000 cm^{-1}) spectrometer. ^{1}H 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.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethylyttriate(III) (1). A suspension of 2.1 g (10.75 mmol) of YCl_3 in 60 mL of diethyl ether and 3.75 g (32.3 mmol) of tmed was treated at −78 °C dropwise with 4.37 mL of a freshly prepared 1.6 M solution of methyllithium in diethyl ether. After being stirred until the addition of methyllithium was finished, the reaction mixture was allowed to warm to 20 °C. After 3 h of further stirring at room temperature, the clear colorless solution was decanted into a Schlenk tube. The solution was cooled to −30 °C overnight, and colorless crystals could be obtained next day by decanting the solvent and careful drying in vacuo: yield 2.1 g (22%) of 1; decomp pt 128–132 °C; IR (Nujol, cm^{-1}) 1295 (s), 1290 (m), 1252 (s), 1178 (s), 1158 (s), 1125 (m), 1109 (sh), 1065 (m), 1039 (m), 1018 (m), 949 (s), 887 (m), 826 (s), 790 (s), 768 (m), 720 (m), 586 (br), 550–380 (br, not resolved). Anal. Calcd for $C_{24}H_{66}Li_3N_6Y$: C, 52.55; H, 12.13; N, 15.32; Y, 16.21. Found: C, 52.51; H, 12.00; N, 14.75; Y, 14.92.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethyllanthanate(III) (2). This compound was prepared from 1.9 g (7.75 mmol) of $LaCl_3$, 2.7 g (23.24 mmol) of tmed, and 31.5 mL of a 1.6 M solution of methyllithium in 60 mL of diethyl ether by using the procedure described above. Colorless crystals of 2 were obtained after three subsequent recrystallizations from diethyl ether–pentane: yield 1.87 g (41%); decomp pt 79–82 °C. Anal. Calcd for $C_{24}H_{66}LaLi_3N_6$: C, 48.16; H, 11.11; La, 23.21; N, 14.04. Found: C, 49.16; H, 12.13; La, 25.04; N, 15.17.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethylpraseodymate(III) (3). This compound was prepared from 3.4 g (13.75 mmol) of $PrCl_3$, 4.8 g (41.25 mmol) of tmed, and 56 mL of a 1.6 M solution of methyllithium in 60 mL of diethyl ether by using the procedure described above. Green crystals of 3 were isolated: yield 5.4 g (65%); decomp pt 59–62 °C; IR (Nujol, cm^{-1}) 1294 (s), 1290 (m), 1252 (s), 1179 (s), 1158 (s), 1125 (m), 1110 (sh), 1064 (m), 1040 (m), 1019 (m), 949 (s), 887 (m), 828 (s), 790 (s), 769 (m), 721 (m), 568 (br), 550–380 (br, not resolved). Anal. Calcd. for $C_{24}H_{66}Li_3N_6Pr$: C, 48.00; H, 11.08; N, 13.99; Pr, 23.36. Found: C, 48.18; H, 11.21; N, 12.84; Pr, 24.70.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) lithium] Hexamethylneodymate(III) (4). The compound was prepared according to 1 from 3.0 g (12.0 mmol) of $NdCl_3$, 4.71 g (35.92 mmol) of tmed, and 48.6 mL of a 1.6 M solution of methyllithium in 60 mL of diethyl ether. After being warmed up and stirred 6 h at room temperature, a violet solution was decanted, which yielded 4.6 g (64%) of 4 following the procedure of 1: decomp pt 78–83 °C; IR (Nujol, cm^{-1}) 1295 (s), 1290 (m), 1254 (s), 1178 (s), 1158 (s), 1125 (m), 1110 (sh), 1065 (m), 1040 (m), 1017 (m), 949 (s), 888 (m), 828 (s), 790 (s), 770 (s), 720 (m), 585 (br), 550–380 (br, not resolved). Anal. Calcd for $C_{24}H_{66}Li_3N_6Nd$: C, 47.73; H, 11.02; N, 13.92; Nd, 23.89. Found: C, 48.20; H, 11.19; N, 12.87; Nd, 20.46.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethylsamarate(III) (5). In an analogous manner to that described for 1, 2.6 g (10.13 mmol) of $SmCl_3$, 3.53 g (30.39 mmol) of tmed, 41.15 mL of a 1.6 M solution of methyllithium in diethyl ether, and 60 mL of diethyl ether yielded 2.9 g (48%) of yellow 5: decomp pt 85–88 °C; IR (Nujol, cm^{-1}) 1290 (s), 1286 (m), 1253 (s), 1178 (m), 1153 (m), 1125 (br), 1100 (sh), 1061 (m), 1035 (m), 1018 (m), 945 (s), 840 (sh), 830 (m), 790 (s), 770 (s), 720 (s), 580 (m), 550–380 (br, not resolved). Anal. Calcd for $C_{24}H_{66}Li_3N_6Sm$: C, 47.25; H, 10.90; N, 13.78; Sm, 24.66. Found: C, 47.59; H, 10.96; N, 12.86; Sm, 24.50.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethylgadolinate(III) (6). In an analogous manner to that described for 1, 3.2 g (12.13 mmol) of $GdCl_3$, 4.23 g (36.41 mmol) of tmed, 49.30 mL of a 1.6 M solution of methyllithium in diethyl ether, and 60 mL of diethyl ether yielded 4.6 g (61%) of light green 6: decomp pt 112 °C; IR (Nujol, $cm-^{1}$) 1292 (s), 1285 (m), 1250 (w), 1175 (sh), 1161 (sh), 1149 (s), 1113 (s), 1086 (sh), 1060 (br), 1030 (m), 940 (m), 840 (w), 810 (sh), 788 (s), 767 (s), 720 (s), 580 (w), 550–380 (br, not resolved). Anal. Calcd for $C_{24}H_{66}GdLi_3N_6$: C, 46.75; H, 10.79; Gd, 25.45; N, 13.63. Found: C, 48.47; H, 11.20; Gd, 24.91; N, 12.68.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethylterbate(III) (7). In an analogous manner to that described for 1, 2.65 g (10 mmol) of $TbCl_3$, 3.49 g (30 mmol) of tmed, 40.63 mL of a 1.6 M solution of methyllithium in diethyl ether, and 50 mL of diethyl ether yielded 2.6 g (41%) of colorless 7: decomp pt 115 °C; IR (Nujol, cm^{-1}) 1292 (s), 1285 (m), 1251 (w), 1180 (m), 1157 (m), 1126 (s), 1105 (s), 1075 (sh), 1038 (m), 1019 (m), 949 (m), 839 (w), 825 (m), 790 (s), 775 (s), 720 (s), 580 (w), 550–380 (br, not resolved). Anal. Calcd for $C_{24}H_{66}Li_3N_6Tb$: C, 46.59; H, 10.75; N, 13.59; Tb, 25.69. Found: C, 44.40; H, 10.22; N, 11.56; Tb, 24.31.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethyldysprosiate(III) (8). In an analogous manner to that described for 1, 3.03 g (11.3 mmol) of $DyCl_3$, 3.94 g (33.9 mmol) of tmed, 45.91 mL of a 1.6 M solution of methyllithium in diethyl ether, and 60 mL of diethyl ether yielded 3.22 g (46%) of colorless 8: decomp pt 106 °C; IR (Nujol, cm^{-1}) 1293 (s), 1287 (m), 1252 (s,) 1183 (m), 1159 (m), 1125 (m), 1105 (m), 1071 (m), 1031 (m), 1018 (m), 950 (m), 841 (w), 828 (m), 790 (s), 775 (s), 720 (s), 580 (w), 550–380 (br, not resolved). Anal. Calcd for $C_{24}H_{66}DyLi_3N_6$: C, 46.34; H, 10.69; Dy, 26.11; N, 13.51. Found: C, 44.64; H, 10.31; Dy, 24.31; N, 13.47.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethylholmiate(III) (9). In an analogous manner to that described for 1, 3.4 g (12.5 mmol) of $HoCl_3$, 4.36 g (37.5 mmol) of tmed, 50.8 mL of a 1.6 M solution of methyllithium in diethyl ether, and 60 mL of diethyl ether yielded 2.9 g (38%) of yellowish crystals of 9: decomp pt 122 °C; IR (Nujol, cm^{-1}) 1295 (s), 1290 (sh), 1255 (s), 1182 (m), 1160 (s), 1125 (m), 1100 (sh), 1070 (m), 1039 (m), 1020 (sh), 955 (s), 840 (w), 820 (w), 790 (s), 780 (m), 722 (s), 590 (w), 550–380 (br, not resolved). Anal. Calcd for $C_{24}H_{66}HoLi_3N_6$: C, 46.15; H, 10.65; Ho, 26.41; N, 13.46. Found: C, 45.34; H, 10.68; Ho, 24.17; N, 12.33.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethylerbate(III) (10). In an analogous manner to that described for 1, 2.2 g (8.0 mmol) of $ErCl_3$, 2.80 g (24.1 mmol) of tmed, 32.6 mL of a 1.6 M solution of methyllithium in diethyl ether, and 50 mL of diethyl ether yielded 2.2 g (44%) of pink crystals of 10: decomp pt 122–125 °C; IR (Nujol, cm^{-1}) 2760 (s), 2710 (sh), 1292 (s), 1288 (s), 1260 (s), 1180 (s), 1159 (s), 1130 (s), 1113 (s), 1065 (s), 1040 (s), 1022 (s), 950 (s), 830 (w), 792 (s), 772 (m), 728 (vw), 589 (m), 530–380 (br, not resolved), 284 (m, br). Anal. Calcd for $C_{24}H_{66}ErLi_3N_6$: C, 46.15; H, 10.65; Er, 26.77; N, 13.46. Found: C, 44.74; H, 10.45; Er, 26.40; N, 13.77.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethylthuliate(III) (11). In an analogous manner to that described for 1, 2.75 g (10 mmol) of $TmCl_3$, 3.48 g (30 mmol) of tmed, 40.6 mL of a 1.6 M solution of methyllithium in diethyl ether, and 60 mL of diethyl ether yielded 2.5 g (40%) of green-yellow crystals of 11, decomp pt 109–114 °C. Anal. Calcd for $C_{24}H_{66}Li_3N_6Tm$: C, 45.86; H, 10.58; N, 13.37; Tm, 26.88. Found: C, 46.36; H, 10.59; N, 12.81; Tm, 25.36.

Tris[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium] Hexamethylytterbate(III) (12). In an analogous manner to that described for 1, 3.5 g (12.5 mmol) of $YbCl_3$, 4.36 g (37.5 mmol) of tmed, 50.8 mL of a 1.6 M solution of methyllithium in diethyl ether, and 60 mL of diethyl ether yielded 2.0 g (26%) yellow crystals of 12: decomp pt 116–126 °C; IR (Nujol, cm^{-1}) 2760 (sh), 1294 (sh), 1287 (sh), 1260 (m), 1180 (m), 1160 (s), 1130 (s), 1115

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Table I. Crystal Data and Data Collection Details for $[Li(tmed)]_3[Ho(CH_3)_6]$ (9)[a]

formula	$C_{24}H_{66}HoLi_3N_6$
mol wt, amu	624.60
space group	$R\bar{3}c$
a, pm	1280.7 (20)
α, deg	79.84 (13)
vol, nm^3	2.012 (22)
Z	2
D(calcd), g/cm^3	0.96
D(found), g/cm^3	0.9
radiation λ, pm	Mo Kα, 71.069
abs coeff, cm^{-1}	18.82
monochromator	graphite
method	ω-2θ
scan speed	variable
two stds after each 50 reflectns	
2θ limit, deg	$5 \leqslant 2\theta \leqslant 60$
no. of reflectns	2815
reflectns obsd	1533, $I \leqslant 2\sigma(I)$
data collectn temp, K	160
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	0.050

[a] Estimated standard deviations in parentheses.

Table II. Positional Parameters for $[Li(tmed)]_3[Ho(CH_3)_6]$ (9)

atom	x/a	y/b	z/c	B_{eq}[a]
Ho	0.25	0.25	0.25	2.44
Li	0.0698 (19)	0.4302 (19)	0.25	2.90
C(1)	0.1260 (15)	0.3409 (12)	0.1130 (13)	3.50
N	0.0498 (10)	0.6003 (9)	0.2098 (10)	3.71
C(20)	0.1041 (23)	0.6283 (17)	0.0995 (29)	3.71
C(30)	0.0795 (26)	0.6605 (24)	0.2833 (30)	5.19
C(40)	−0.0700 (26)	0.6306 (25)	0.2020 (22)	4.03
C(21)	0.0686 (28)	0.6416 (29)	0.0935 (23)	5.49
C(31)	0.1170 (23)	0.6430 (20)	0.2700 (22)	3.52
C(41)	−0.0645 (28)	0.6289 (25)	0.2616 (33)	4.75

[a] $B_{eq} = {}^1/_3 \Sigma_i \Sigma_j B_{ij} a_i^* a_j^* a_i a_j$.

(s), 1100 (m), 1065 (m), 1038 (s), 1021 (s), 950 (s), 792 (s), 772 (m), 728 (w), 588 (m), 530–380 (br, not resolved), 245 (m, br). Anal. Calcd for $C_{24}H_{66}Li_3N_6Yb$: C, 45.56; H, 10.52; N, 13.28; Yb, 27.35. Found: C, 48.46; H, 11.22; N, 13.26; Yb, 28.68.

Tris[(*N*,*N*,*N′*,*N′*-tetramethylethylenediamine)lithium] Hexamethyllutetate(III) (13). In an analogous manner to that described for **1**, 3.3 g (11.8 mmol) of $LuCl_3$, 4.11 g (35.4 mmol) of tmed, 47.9 mL of a 1.6 M solution of methyllithium in diethyl ether, and 60 mL of diethyl ether yielded 3.7 g (50%) of colorless **13**: decomp pt 142 °C; IR (Nujol, cm^{-1}) 2760 (s), 2710 (sh), 1288 (sh), 1280 (sh), 1260 (m), 1181 (m), 1160 (s), 1130 (s), 1115 (s), 1100 (m), 1065 (m), 1040 (s), 1023 (s), 951 (s), 830 (w), 792 (s), 772 (m), 725 (w), 585 (m), 530–380 (br, not resolved), 250 (m, br). Anal. Calcd for $C_{24}H_{66}Li_3LuN_6$: C, 45.42; H, 10.48; Lu, 27.57; N, 13.24; Found: C, 45.70; H, 10.57; Lu, 27.19; N, 12.87.

Bis(*N*,*N*,*N′*,*N′*-tetramethylethylenediamine)lithium Tetra-*tert*-butylterbate(III) (14). A 1.36 g (5.12 mmol) sample of $TbCl_3$ was suspended in 60 mL of diethyl ether and the mixture cooled to −30 °C. A 12.8-mL sample of a 1.6 M solution of *tert*-butyllithium in pentane (20.5 mmol) was added with a dropping funnel. After 2 h of stirring, the mixture was warmed to room temperature. The colorless precipitate was filtered, and 1.22 g (10.5 mmol) of tmed was added to the remaining solution. The resulting reaction mixture was concentrated to 20 mL, and pentane was added to precipitate **14**, which was filtered, washed twice with pentane, and dried in vacuo; yield 1.1 g (34%) of **14**. Anal. Calcd for $C_{28}H_{68}LiN_4Tb$: Tb, 25.36. Found: Tb, 25.07.

Tetrakis(diethyl ether)lithium Tetra-*tert*-butylerbate(III) (15). A 1.40-g (5.12-mmol) sample of $ErCl_3$ was suspended in 60 mL of diethyl ether and the mixture cooled to −30 °C. A 12.8-mL sample of a 1.6 M solution of *tert*-butyllithium in pentane (20.5 mmol) was added with a dropping funnel. After 2 h of stirring, the mixture was warmed to room temperature. The pink solution was filtered, the precipitate was washed with diethyl ether, and the combined solutions were concentrated to 20 mL. Addition of about 50 mL of pentane resulted in the precipitation of a pink powder, which was recrystallized twice from diethyl ether–pentane and dried in vacuo; yield 1.36 g (38%) of **15**. Anal. Calcd for $C_{32}H_{76}ErLiO_4$: Er, 23.92. Found: Er, 23.96.

Bis(*N*,*N*,*N′*,*N′*-tetramethylethylenediamine)lithium Tetra-*tert*-butyllutetate(III) (16). A 1.94-g (4.94-mmol) sample of $Lu(OCMe_3)_3$ diluted in 40 mL of pentane and 12.2 g (10.5 mmol) of tmed were treated with 9.25 mL of a 1.6 M solution of *tert*-butyllithium in pentane (14.8 mmol). After the solution was stirred for 2 h, a white precipitate resulted, which was filtered and washed three times with diethyl ether–pentane and dried, to yield 0.75 g (24%) of **16**: decomp pt 95 °C; IR (Nujol, cm^{-1}) 2750 (s), 2720 (s), 2670 (s), 1360 (s), 1290 (s), 1248 (m), 1218 (m), 1207 (sh), 1184 (m), 1160 (s), 1138 (s), 1130 (s), 1098 (m), 1070 (m), 1045 (w), 1031 (s), 1016 (s), 988 (m), 972 (w), 950 (s), 790 (sh), 780 (s), 775 (sh), 740 (w), 725 (w), 590 (m), 486 (s) 475 (s), 440 (m), 345 (m, br); ^1H NMR (THF-d_8; ppm relative Me_4Si) 0.97 (CCH_3), 2.13 (NCH_3), 2.27 (NCH_2). Anal. Calcd for $C_{28}H_{68}LiLuN_4$: Li, 1.08; Lu, 27.22. Found: Li, 1.65; Lu, 27.36.

X-ray Analysis of 9. A yellowish crystal of **9** with the dimensions 0.25 × 0.35 × 0.35 mm was placed in a thin-walled glass capillary and sealed under argon. Intensities were measured on a Syntex four-circle $P2_1$ diffractometer. The crystal data and some data collection details are given in Table I. The observed reflections were corrected for Lorentz and polarization effects but not for absorption. Atomic scattering factors and anomalous dispersion terms for the holmium atom were taken from ref 18.

Solution and Refinement of the Structure. The number of molecules in the unit cell was calculated after the pycnometric determination of the density to be $Z = 2$. Of the possible rhombohedric space groups $R3c$ and $R\bar{3}c$ the latter was chosen. The successful solution of the structure proved this choice to be right. The structure was solved by Patterson methods. The holmium atom occupies the special position 2a with coordinates $^1/_4$, $^1/_4$, $^1/_4$. The positional parameters of the carbon atoms could be obtained from a Patterson map. Successive Fourier and difference Fourier syntheses showed the positions of all the other non-hydrogen atoms. The structure was refined by use of the full-matrix least squares using the SHELX program.[19] The minimized function is $\sum w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values according to the expression $w = 1/\sigma(F_o)^2$. The structure was refined to an R factor of 0.078, but the C–C distance of tmed was only 132 pm, far below the normal 154 pm, and the thermal parameters of the carbon atoms were very high. Therefore solutions in space groups $R3m$, $R\bar{3}m$, and $R3c$ were tried too but gave even worse results. Therefore a disorder was postulated, as in (triphenylmethyl)lithium tetramethylethylenediamine, described by Brooks and Stucky.[20] The positions of the hydrogens of tmed were calculated and incorporated to the data set with a fixed temperature factor of $U = 600$ pm^2 (the difference Fourier synthesis showed electron density possible due to the hydrogens in the area of the carbons C(1), but these hydrogen positions could not be refined). A final difference Fourier synthesis did not show any remarkable features. The final R factor was 0.050.

The final values of the parameters for **9** are reported in Table II. Observed and calculated structure factors are available as supplementary material.

Results and Discussion

Synthesis of Hexamethyl and Tetra-*tert*-butyl Derivatives of the Rare Earths. Dropwise addition of an etheral solution of methyllithium to a suspension of yttrium trichloride, lanthanum trichloride, and the trichlorides of the lanthanides with the exception of $CeCl_3$, $PmCl_3$, and $EuCl_3$ in diethyl ether in the presence of a stochiometric amount of *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (tmed) results in the formation of the appropriate tris[(*N*,*N*,*N′*,*N′*-tetramethylethylenediamine)lithium]

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(18) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2.A and 2.3.1.

(19) Sheldrick, G. M. "SHELX-76 System of Programs", 1976.

(20) Brooks, J. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7333.

Table III. Yields, Colors, and Decomposition Points for Compounds $[Li(tmed)]_3[Ln(CH_3)_6]$ and $Li(tmed)_2[Ln(t\text{-}C_4H_9)_4]$

compound	yield, %	color	decomp pt, °C
$[Li(tmed)]_3[Y(CH_3)_6]$ (1)	22	colorless	128-132
$[Li(tmed)]_3[La(CH_3)_6]$ (2)	41	colorless	79-82
$[Li(tmed)]_3[Pr(CH_3)_6]$ (3)	65	green	59-62
$[Li(tmed)]_3[Nd(CH_3)_6]$ (4)	64	violet	78-83
$[Li(tmed)]_3[Sm(CH_3)_6]$ (5)	48	yellow	85-88
$[Li(tmed)]_3[Gd(CH_3)_6]$ (6)	61	light green	112
$[Li(tmed)]_3[Tb(CH_3)_6]$ (7)	41	colorless	115
$[Li(tmed)]_3[Dy(CH_3)_6]$ (8)	46	colorless	106
$[Li(tmed)]_3[Ho(CH_3)_6]$ (9)	38	yellowish	122
$[Li(tmed)]_3[Er(CH_3)_6]$ (10)	44	pink	122-125
$[Li(tmed)]_3[Tm(CH_3)_6]$ (11)	40	green-yellow	109-114
$[Li(tmed)]_3[Yb(CH_3)_6]$ (12)	26	yellow	116-126
$[Li(tmed)]_3[Lu(CH_3)_6]$ (13)	50	colorless	142
$Li(tmed)_2[Tb(t\text{-}C_4H_9)_4]$ (14)	34	colorless	>50
$Li(Et_2O)_4[Er(t\text{-}C_4H_9)_4]$ (15)	38	pink	>40
$Li(tmed)_2[Lu(t\text{-}C_4H_9)_4]$ (16)	24	colorless	95

hexamethylmetalate(III) derivatives (eq 1).

$$LnCl_3 + 6LiCH_3 + 3tmed \xrightarrow[-78\ °C]{Et_2O} \underset{1-13}{[Li(tmed)]_3[Ln(CH_3)_6]} + 3LiCl \quad (1)$$

Starting the reaction at −78 °C and stirring at room temperature for 2 h after complete addition of methyllithium gave yields between 22 and 65% (see Table III). The air-sensitive complexes are obtained as crystalline powders after precipitation with pentane and subsequent recrystallization from ether–pentane. They are soluble in diethyl ether and tetrahydrofuran and slightly soluble in benzene and toluene but insoluble in saturated hydrocarbons such as pentane. The thermal stability depends upon the particular rare-earth metal. All compounds decompose without melting. The yttrium derivative and the methyl derivatives of the heavier lanthanides are more stable than those of the lighter ones, according to the crystal radii of the ions Ln^{3+}. The smallest ions Lu^{3+} (84.8 pm),[21] Yb^{3+} (85.8),[21] Tm^{3+} (86.9),[21] Er^{3+} (88.1),[21] Ho^{3+} (89.4),[21] and Y^{3+} (88)[22] give complexes that decompose above 120 °C, all the other larger ions form complexes that are less stable. The praseodymium complex ignites spontaneously in air.

The reaction of $ScCl_3$ and $CeCl_3$ with methyllithium and tmed in diethyl ether did not yield pure products. $EuCl_3$ was reduced immediately by methyllithium. An organometallic compound of this rare-earth metal could not be isolated.

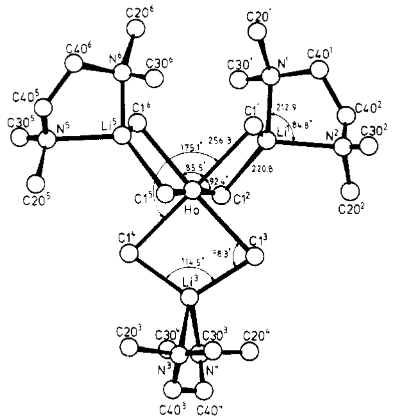

Figure 1. PLUTO drawing of the molecule $[Li(tmed)]_3[Ho(CH_3)_6]$ (**9**) (hydrogen atoms are omitted).

$TbCl_3$, $ErCl_3$, and $LuCl_3$ react in pentane in the presence of diethyl ether with *tert*-butyllithium independent of the molar ration of the starting materials to form unstable complexes with ether as stabilizing ligands. The use of tmed allows the isolation of very sensitive compounds of the type $[Li(tmed)_2][Ln(t\text{-}C_4H_9)_4]$ (eq 2 and 3).

$$LnCl_3 + 4Li(t\text{-}C_4H_9) + 4Et_2O \xrightarrow[-30\ °C]{pentane} [Li(Et_2O)_4][Ln(t\text{-}C_4H_9)_4] + 3LiCl \quad (2)$$

$$Ln = Tb, Er, Lu$$

$$LnCl_3 + 4Li(t\text{-}C_4H_9) + 2tmed \xrightarrow[-30\ °C]{pentane} [Li(tmed)_2][Ln(t\text{-}C_4H_9)_4] + 3LiCl \quad (3)$$

$$Ln = Tb, Er, Lu$$

Interaction of lutetium *tert*-butoxide with *tert*-butyllithium in pentane in the presence of tmed at room temperature gave colorless bis(*N*,*N*,*N′*,*N′*-tetramethylethylenediamine)lithium tetra-*tert*-butyllutetate(III), which showed the expected bands in the IR spectrum[7] (eq 4).

$$Lu(O\text{-}t\text{-}C_4H_9)_3 + 4Li(t\text{-}C_4H_9) + 2tmed \xrightarrow{pentane} 3LiO\text{-}t\text{-}C_4H_9 + \underset{16}{[Li(tmed)_2][Lu(t\text{-}C_4H_9)_4]} \quad (4)$$

Spectroscopic Characterization. All new compounds except those with Y, La, and Lu are paramagnetic, and therefore, we could not obtain acceptable NMR spectra of **6**–**11** as well as of **14** and **15**. The diamagnetic yttrium, lanthanum, and lutetium derivatives **1**, **2**, and **13**, respectively, show in benzene-d_6–diethyl ether the expected ^1H and ^{13}C signals for the methyl groups and the tmed ligands (Table IV). The spectra of the weakly paramagnetic compounds of praseodynium (**3**), neodymium (**4**), and samarium (**5**) showed broadened signals with half-widths of the methyl peaks between 15 and 48 Hz. In the ^{13}C NMR spectra there could be found no signals for the metal-bonded methyl groups of the compounds **3**–**12**, neither at room temperature nor at −78 °C. The half-widths of the YCH_3 signal of **1** was 8 Hz, which may be due to a ^{89}Y ^{13}C coupling.

The ^1H NMR spectrum of the *tert*-butyl complex **16** shows at room temperature and in THF-d_8 singlets at 0.97 (CCH_3), 2.13 (NCH_3), and 2.27 ppm (NCH_2), relative to tetramethylsilane.

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[21] Templeton, D. H.; Dauben, C. H. *J. Am. Chem. Soc.* **1954**, *76*, 5237.

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[24] Gysling, H.; Tsutsui, M. *Adv. Organomet. Chem.* **1970**, *9*, 361.

Table IV. ^{1}H and ^{13}C NMR Spectra Data for [Li(tmed)]$_3$[Ln(CH$_3$)$_6$]^a in C$_6$D$_6$-Diethyl Ether

compound	μ_{eff}^{b}	δ(CH$_3$)	δ(NCH$_2$)	δ(NCH$_3$)	δ(^{13}CH$_3$)	δ(^{13}CH$_2$N)	δ(^{13}CH$_3$N)
[Li(tmed)]$_3$[Y(CH$_3$)$_6$] (**1**)	0	−0.52 (5.3)	2.1	2.26	5.9	57.3	46.3
[Li(tmed)]$_3$[La(CH$_3$)$_6$] (**2**)	0	−0.33 (1.5)	1.95	2.24	17.8	57.1	46.2
[Li(tmed)]$_3$[Pr(CH$_3$)$_6$] (**3**)	3.47	−5.9 (48)	5.1	5.4		61	49.3
[Li(tmed)]$_3$[Nd(CH$_3$)$_6$] (**4**)	3.52	−6.2 (44)	3.5	3.7		60	49.0
[Li(tmed)]$_3$[Sm(CH$_3$)$_6$] (**5**)	1.58	−2.8 (16)	2.6	2.9		58	46.8
[Li(tmed)]$_3$[Gd(CH$_3$)$_6$] (**6**)	7.9						
[Li(tmed)]$_3$[Tb(CH$_3$)$_6$] (**7**)	9.6	−108 (400)	2.5	5.2			
[Li(tmed)]$_3$[Dy(CH$_3$)$_6$] (**8**)	10.3	−74 (600)				58.1	46.8
[Li(tmed)]$_3$[Ho(CH$_3$)$_6$] (**9**)	10.4	−60 (1000)	−3 to +10				
[Li(tmed)]$_3$[Er(CH$_3$)$_6$] (**10**)	9.4		−20 to +20				
[Li(tmed)]$_3$[Tm(CH$_3$)$_6$] (**11**)	7.0	92 (1200)	−40 to +20				
[Li(tmed)]$_3$[Yb(CH$_3$)$_6$] (**12**)	4.3					55.1	44.1
[Li(tmed)]$_3$[Lu(CH$_3$)$_6$]^c (**13**)	0	−1.18 (3.5)	2.23	2.30	4.5	58.2	45.9

^{a} Chemical shifts are reported in ppm from Si(CH$_3$)$_4$; in parentheses are the line widths at half-maximum. ^{b} Observed μ_{eff} (μ_B) of Ln$_2$(SO$_4$)$_3$·(H$_2$O)$_8$.[24] ^{c} In diethyl ether.

Table V. Selected Bond Lengths^a (pm) and Angles^a (deg) for [Li(tmed)]$_3$[Ho(CH$_3$)$_6$] (**9**) and [Li(tmed)]$_3$[Er(CH$_3$)$_6$] (**10**)[15]

9		**10**	
Ho–C(1)	256.3 (18)	Er–C(1)	257 (2)
Li–C(1)	220.8 (18)	Li–C(1)	222 (4)
Li–N	212.9 (16)	Li–N	221 (4)
N–C(20)	147.3 (34)	N–C(20)	152 (4)
N–C(30)	145.3 (43)	N–C(30)	145 (3)
N–C(40)	153.1 (36)	N–C(40)	138 (4)
C(40)^1–C(40)^2	150.1 (57)	C(40)^1–C(40)^2	152 (5)
N–C(21)	148.2 (31)		
N–C(31)	147.9 (36)		
N–C(41)	150.5 (36)		
C(41)^1–C(41)^2	142.7 (77)		
C(1)^1–Ho–C(1)^2	92.4 (8)	C(1)^1–Er–C(1)^2	93 (1)
C(1)^1–Ho–C(1)^3	91.2 (8)		
C(1)^1–Ho–C(1)^4	175.1 (8)		
C(1)^1–Ho–C(1)^5	91.2 (8)		
C(1)^1–Ho–C(1)^6	85.5 (8)		
Ho–C(1)–Li	76.3 (6)	Er–C(1)–Li	77 (2)
C(1)^1–Li–C(1)^2	114.5 (9)	C(1)^1–Li–C(1)^2	114 (2)
N^1–Li–N^2	84.8 (10)	N^1–Li–N^2	86 (2)
C(1)–Li–N	115.0 (5)	C(1)–Li–N	111 (2)

^{a} Estimated standard deviations in parentheses; symmetry code: 1, x, y, z; 2, $1/2 - y$, $1/2 - x$, $1/2 - z$; 3, z, x, y; 4, $1/2 - z$, $1/2 - y$, $1/2 - x$; 5, y, z, x; 6, $1/2 - x$, $1/2 - z$, $1/2 - y$.

The infrared spectra of the various compounds show the expected vibrations for the methyl, *tert*-butyl, and tmed ligands. A reliable assignment of rare earth-to-carbon bond stretching vibrations was not possible.

Molecular Structure of [Li(tmed)]$_3$[Ho(CH$_3$)$_6$] (9) and [Li(tmed)]$_3$[Er(CH$_3$)$_6$] (10).[15] The molecular structure and atom numbering scheme of compound **9** is shown in Figure 1. Some important structural features are listed in Table V together with those of the erbium derivative **10**.[15] Both compounds consist of monomeric units in which the lanthanide metal is surrounded by six methyl groups in a slightly distorted octahedral arrangement (the symmetry of the molecule is D_3). The holmium atom occupies the special position 2a. The lithium atoms are located at special positions 6e at the centers of tetrahedra made up of two methyl groups and the two nitrogen atoms of one tmed ligand. Thus the octrahedron is connected to three tetrahedra in a way that each tetrahedron shares one common edge with the octahedron. The CH$_3$^{1}–Ln–CH$_3$^{2} angles are widened to 92.4° in **9** and to 93° in **10**.

The lithium-centered tetrahedra can be arranged around the central octahedron in two ways. Thus there exist two possibilities for the monomeric molecules, which are both present as optical antipodes in one unit cell. In Figure 2 the relative positions of the tmed ligands are indicated by black dashes, in order to illustrate the left-hand helix of one and the right-hand helix of the other formula unit. The structure of **9** shows a disorder of the tmed ligands. The nitrogen atoms occupy fixed positions, but the carbon atoms rotate around the Li–N axes. Figure 3 shows both arrangements. The rotation angle C(20)–N–C(21) is 19°.

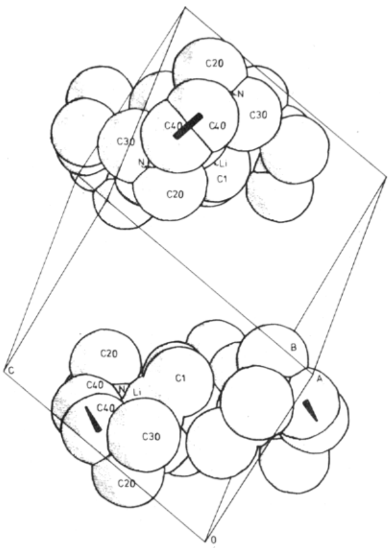

Figure 2. Arrangement of the optical antipodes in the unit cell of [Li(tmed)]$_3$[Ho(CH$_3$)$_6$] (**9**).

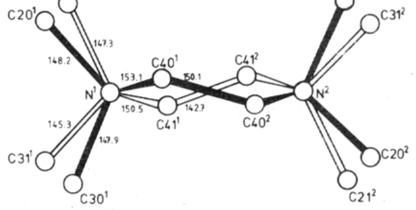

Figure 3. PLUTO drawing and atom numbering of the tmed ligands in [Li(tmed)]$_3$[Ho(CH$_3$)$_6$] (**9**), showing the two different arrangements of the tmed ligand in relation to the L–N axis.

In the two examples **9** and **10** the permethylated lanthanides exhibit identical structures. The rare-earth metals are surrounded by six methyl groups with Ln–C distances of 256.3 (Ho–C) and 257 pm (Er–C). This is in accordance with Ln–C distances in other electron-deficient organolanthanides: the bond length Yb–C in Cp$_2$Yb(μ-CH$_3$)$_2$YbCp$_2$ is 254 pm[25] and in Cp$_2$Yb(μ-CH$_3$)$_2$Al(CH$_3$)$_2$

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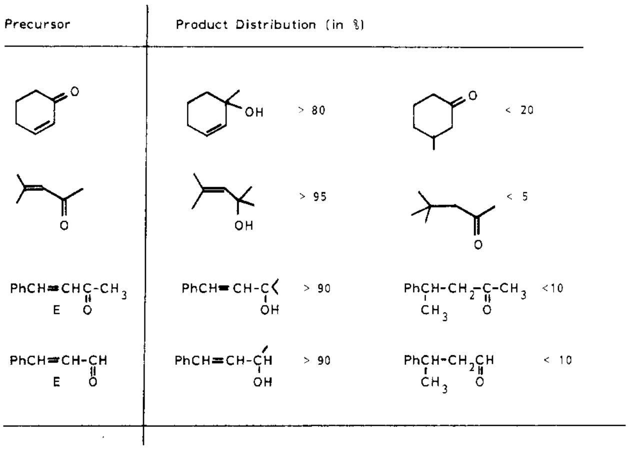
(25) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 480.

Chart I. Methylation of α,β-Unsaturated Aldehydes and Ketones by 3 and 5



253 pm,[26] whereas compounds like $Cp_2LuCH_2SiMe_3\cdot(THF)$[27] and $Cp_2LuC_6H_4CH_3\cdot(THF)$[27] show significantly shorter Lu–C distances of 237 and 234 pm, respectively.

Reactivity. The new compounds are extremely sensitive toward moisture and oxygen. On hydrolysis all the ligands are replaced from the rare earths with concurrent formation of $Ln(OH)_3$, CH_4, and tmed, respectively; in the case of **14**, **15**, and **16** LiOH and C_4H_{10} were formed additionally. To explore the reactivity of the complexes in the methylation of α,β-unsaturated ketones and aldehydes, some preliminary experiments were carried out with **3** and **5**. Whereas cyclohexen-2-one yields the 1,2 and 1,4 addition products in a ratio 4:1 (determined by GC/MS), for 2-methylbuten-3-one, benzalacetone, and cinnamic aldehyde the 1,2 methylation adducts are formed in more than 90% yields (Chart I). The overall yields for the methylation (not optimized) is >80 %. For a test of the chemoselectivity of the rare-earth complexes, a 1:1 mixture of benzalacetone and cinnamic aldehyde (each 3 mmol) was treated with 4.1 mmol of **3** or **5** and it was observed that methylation of the aldehyde is favored by a ratio of approximately 1.5–2.0:1.

Typical experimental conditions for the methylation are as follows: 25 mmol of benzalacetone is dissolved in 40 mL of THF (dried over potassium) and the mixture cooled down to −78 °C. Under argon atmosphere a solution of 4.2 mmol of **3** in 30 mL of Et_2O (dried over NaH) is added slowly, and the reaction mixture is stirred for 2 h at −78 °C. Hydrolysis is carried out by adding a saturated NH_4Cl solution, followed by addition of 5% HCl until a pH of 3 is reached. The organic compounds are isolated by extraction with CH_2Cl_2 and identified by ^1H NMR, IR, and GC/MS spectroscopy, respectively.

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Registry No. **1**, 87615-28-9; **2**, 87639-03-0; **3**, 76206-86-5; **4**, 76206-88-7; **5**, 76206-90-1; **6**, 87615-30-3; **7**, 87615-32-5; **8**, 87615-34-7; **9**, 87615-36-9; **10**, 66862-11-1; **11**, 76206-92-3; **12**, 76206-94-5; **13**, 66862-13-3; **14**, 87615-38-1; **15**, 87615-40-5; **16**, 87615-42-7; YCl_3, 10361-92-9; $LiCH_3$, 917-54-4; tmed, 110-18-9; $LaCl_3$, 10099-58-8; $PrCl_3$, 10361-79-2; $NdCl_3$, 10024-93-8; $SmCl_3$, 10361-82-7; $GdCl_3$, 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; Li-*t*-C_4H_9, 594-19-4; $Lu(OCMe_3)_3$, 87615-43-8; 2-cyclohexen-1-one, 930-68-7; 4-methyl-3-penten-2-one, 141-79-7; (*E*)-4-phenyl-3-buten-2-one, 1896-62-4; (*E*)-3-phenyl-2-propenal, 14371-10-9; 1-methyl-2-cyclohexen-1-ol, 23758-27-2; 3-methylcyclohexanone, 591-24-2; 2,4-dimethyl-3-penten-2-ol, 56763-70-3; 4,4-dimethyl-2-pentanone, 590-50-1; 2-methyl-4-phenyl-3-buten-2-ol, 25625-21-2; 4-phenyl-2-pentanone, 17913-10-9; 4-phenyl-3-buten-2-ol, 17488-65-2; 3-phenylbutanal, 16251-77-7.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen positions, and additional bond lengths and angles for compound **9** as well as tables of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(26) Holton, J.; Lappert, M. F.; Scollary, G. R.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 425.

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