# Some Novel Halide- and Alkyl-derivatives of Pentamethylcyclopentadienyllanthanum, -praseodymium, -ytterbium and -lutetium*

ILSE ALBRECHT, EKKEHARDT HAHN, JOACHIM PICKARDT and HERBERT SCHUMANN

*Institut fur Anorganische und Analytische Chemie, Technische Universitat Berlin, Berlin 12, F.R.G.*

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## Abstract

$LaCl_3$ and $PrCl_3$ react with $NaC_5Me_5$ or $KC_5Me_5$ in tetrahydrofuran in the presence of ether or dimethoxyethane (dme) to form the new complexes $(C_5Me_5)_2La(\mu\text{-}Cl)_2K(L_2)$, $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(L_2)$ (L = $Et_2O$, dme) and, $C_5Me_5PrCl_3Na(Et_2O)$. These compounds react with $LiCH_3$ or $LiCH_2SiMe_3$ forming new alkyl derivatives of the type $(C_5Me_5)_2Ln(\mu\text{-}CH_3)_2Li(tmed)$ (Ln = La, Lu, tmed = tetramethylethylenediamine), $[Li(dme)_3][(C_5Me_5)_2Lu(CH_2SiMe_3)_2]$ and $[Li(tmed)_2][C_5Me_5Ln(CH_3)_3]$ (Ln = Yb, Lu). The structure of $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$ was determined by X-ray diffraction.

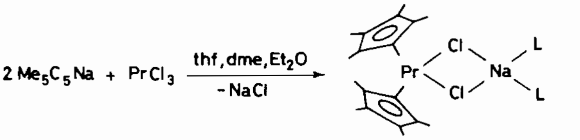
## Introduction

For all lanthanoids, compounds of the type $(C_5H_5)_3Ln$ have been synthesized but complexes with two cyclopentadienyl groups are only known for the heavier lanthanoids [1]. Using pentamethylcyclopentadienyl as a bulky substituted cyclopentadienyl ligand, Tilley and Andersen [2] as well as Wayda and Evans [3] succeeded in preparing bis(pentamethylcyclopentadienyl) derivatives of neodymium. We wish to report the synthesis and characterization of the corresponding compounds of two earlier elements of the lanthanoid series.

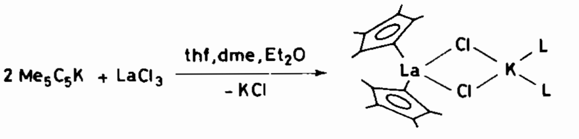
## Results and Discussion

### *Pentamethylcyclopentadienyllanthanum- and praseodymium Chlorides*

Praseodymiumtrichloride reacts in tetrahydrofuran with pentamethylcyclopentadienylsodium in the molar ratio 1:2 to give the compounds $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(L_2)$ with L = $Et_2O$ or dme. Attempts to prepare the corresponding lanthanum complex in the same manner were unsuccessful. However by using pentamethylcyclopentadienyl potassium it was possible to synthesize the lanthanum compounds:



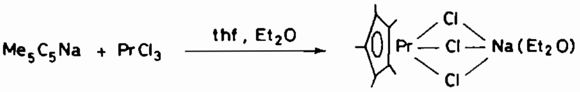
1 (L = dme), 2 (L = $Et_2O$)



3 (L = dme), 4 (L = $Et_2O$)

The lanthanum complexes **3** and **4** are obtained in low yields (10–15%) as colorless crystals after recrystallization from dme or ether. The praseodymium derivatives **1** and **2** which are light green in color, crystallize better than the lanthanum derivatives with yields up to 55%. The compounds have been characterized by complete elemental analysis [4].

Equimolar amounts of pentamethylcyclopentadienylsodium and $PrCl_3$ react in diethylether–tetrahydrofuran with formation of a mono(pentamethylcyclopentadienyl)praseodymium trichloride complex:



The NMR spectra of the lanthanum compound **4** show only small shifts of the $^1H$ and $^{13}C$ signals in comparison with the corresponding signals of the previously reported complex $(C_5Me_5)_2Lu(\mu\text{-}Cl)_2Li(Et_2O)_2$ [5], which is also diamagnetic. The $^1H$ NMR spectrum of **4** shows a singlet at 2.05 ppm for the $C_5Me_5$ protons, and in the $^{13}C$ NMR spectrum there are signals at 11.3 ($C_5(CH_3)_5$) and 118.63 ppm ($C_5(CH_3)_5$).

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TABLE I. $^1H$ NMR Data for $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$ (1) and $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(Et_2O)_2$ (2) as a Function of Temperature ($\delta$ in ppm, 80 MHz, in thf-$d_8$).

| $T$(°C) | $\delta C_5Me_5$ (1) | $\delta CH_3$ (1) | $\delta CH_2$ (1) | $\delta C_5Me_5$ (2) |
|---|---|---|---|---|
| −80 | 15.77 | 1.03 | 0.83 | 16.2 |
| −70 | 14.78 | 1.04 | 1.04 | |
| −65 | 14.35 | 1.1 | 1.18 | |
| −50 | 12.98 | 1.53 | 1.94 | |
| −30 | | | | 12.5 |
| −24 | 11.16 | 2.3 | 2.92 | |
| 0 | 9.77 | 2.65 | 3.19 | 10.7 |
| 30 | 8.7 | 2.82 | 3.27 | 9.5 |
| 78 | | | | 7.9 |

The praseodymium compounds 1 and 2 are paramagnetic. Therefore the resonance signals in the $^1H$ NMR spectrum are broadened in comparison to the corresponding diamagnetic compounds of La or Lu and are tremendously shifted. For the resonance signals of the protons of the $C_5Me_5$ groups a downfield shift could be observed, whereas the signals of the coordinated solvent in compound 1 are shifted to higher field. Table I shows the temperature dependence of the chemical shift in the $^1H$ NMR spectra of 1 and 2.

The praseodymium complex 1 crystallizes in the orthorhombic space group $P2_1ca$ (non-standard setting of $Pca2_1$, No. 29) with $a$ = 16.032(11) Å, $b$ = 16.503(6) Å, $c$ = 25.084(9) Å, $V$ = 6636.6 Å$^3$, $Z$ = 8 and $\rho_{calcd}$ = 1.372 g/cm$^3$. The structure was solved from 4345 unique reflections collected at 138(2) K with $1° \leqslant 2\theta \leqslant 44.4°$. 3240 reflections ($I \geqslant 3\sigma(I)$) were included in the least-squares sums leading to a preliminary $R$ value of 0.0481 ($R_w$ = 0.0613) (Fig. 1).

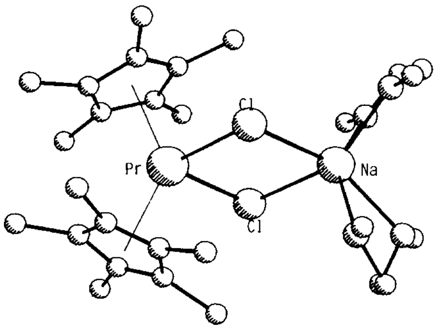


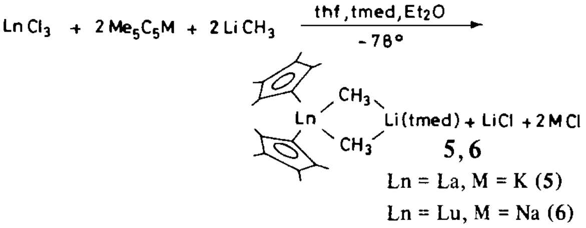
Fig. 1. One of the two molecules per asymmetric unit in the structure of $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$.

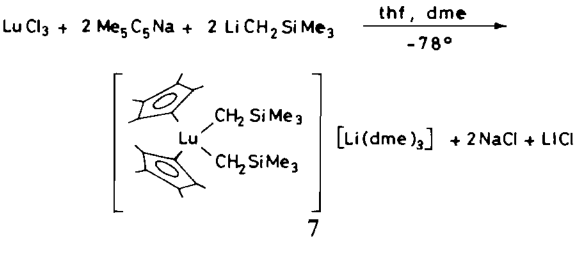
1 is the first bis(pentamethylcyclopentadienyl)-praseodymium chloride complex. A dicyclopentadienylmetal halide complex of Pr has until now only been obtained with the very bulky bis(trimethylsilyl)cyclopentadienyl ligand. This complex [6] is a dimer with two chlorine bridges between the metal centers, whereas 1 is a sodium chloride adduct of $(C_5Me_5)_2PrCl$.

The praseodymium atom is coordinated in a distorted tetrahedral fashion by the centroids of two pentamethylcyclopentadienyl ligands and the two chlorine atoms. The sodium atom resides at the center of a distorted octahedron, formed by two chlorine and four oxygen atoms of the dme ligands. The average Pr-$C_{\eta^5}$ distance of 2.78 Å compares very well with the distance observed for $[\{(Me_3Si)_2C_5H_3\}_2PrCl]_2$ (2.76 Å). The Pr–$Cl_{(ave)}$ separation, however differs for these two complexes (2.734 Å for $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(dme)_2$ *vs.* 2.81 Å for the bis(trimethylsilyl)cyclopentadienyl compound). Other important molecular parameters for 1 are Cp–Pr–$Cp_{(ave)}$ = 135.2°, Pr–Cl–$Na_{(ave)}$ = 93.1°, Cl–Pr–$Cl_{(ave)}$ = 83.1°.

### *Pentamethylcyclopentadienyllanthanum and -lutetium Alkyl Derivatives*

$LaCl_3$ or $LuCl_3$ react with pentamethylcyclopentadienylsodium or -potassium and methyllithium or trimethylsilylmethyllithium in tetrahydrofuran in the presence of tetramethylethylenediamine (tmed) or dme at −78 °C with formation of bis(pentamethylcyclopentadienyl)lanthanoid dialkyllithium complexes, which are stabilized by tmed or dme:

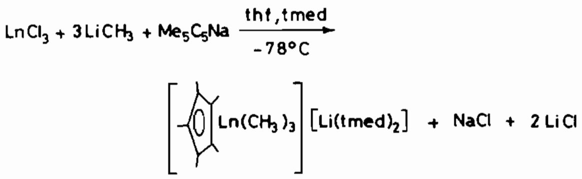




$YbCl_3$ or $LuCl_3$ react under the same conditions with an equimolar amount of $Me_5C_5Na$ and four equivalents of methyllithium only with formation of the homoleptic complexes $[Li(tmed)]_3[LnMe_6]$, which can be prepared by other routes [7]. We have been successful in synthesizing and characterizing by an X-ray structure the first monocyclopentadienyl trialkyl derivatives of the lanthanoids by the reaction of $LnCl_3$ (Ln = Yb, Lu) with $Me_5C_5Na$ and $CH_3Li$ in a molar ratio of 1:1:3 in the presence of tmed:

TABLE II. $^1$H and $^{13}$C NMR Data for $(C_5Me_5)_2La(\mu\text{-}CH_3)_2Li(tmed)$ (5), $(C_5Me_5)_2Lu(\mu\text{-}CH_3)_2Li(tmed)$ (6), $(C_5Me_5)_2Lu(CH_2SiMe_3)_2Li(dme)_3$ (7) and $C_5Me_5Lu(CH_3)_3Li(tmed)_2$ (9). δ in ppm, 80 or 20.149 MHz, thf-$d_8$.

| $^1$H NMR | 5 | 6 | 7 | 9 |
|---|---|---|---|---|
| $\delta C_5Me_5$ | 1.97 | 1.93 | 1.88 | 2.05 |
| $\delta CH_2$ | | | −1.86 | |
| $\delta CH_3$ | −1.43 | −1.77 | −0.11 | −1.34 |
| δ(tmed/dme) | 2.25/2.4 | 2.28/2.44 | 3.26/3.42 | 2.29/2.44 |
| $^{13}$C NMR | | | | |
| $\delta C_5Me_5$ | 115.91 | 111.2 | 112.39 | 112.57 |
| $\delta C_5(CH_3)_5$ | 11.11 | 12.1 | 12.76 | 11.23 |
| $\delta CH_2$ | | | 25.87 | |
| $\delta CH_3$ | 25.83 | 22.2 | 6.27 | 28.7 |
| δ(tmed/dme) | 45.88/58.26 | 46.0/58.8 | 58.79/72.55 | 45.79/58.1 |



(8,9)

Ln = Yb (8), Lu (9)

The extremely sensitive compounds can be recrystallized from diethyl ether. The $^1$H and $^{13}$C NMR spectra of 5, 6, 7 and 9 show the expected singlet signals (Table II). Compounds 5 and 6 are neutral complexes in ether with two $CH_3$-bridges between the lanthanoid and lithium, as shown by X-ray structural analysis with $(C_5H_5)_2Er(\mu\text{-}CH_3)_2Li(tmed)$ [8]. We predict an ionic formulation for 7 because of the bulky trimethylsilylmethyl ligands as well as for 8 and 9. The X-ray structural analysis of 9 [9] proves this prediction (Fig. 2), showing a tetrahedrally coordinated lutetium atom. Three unequally bonded methyl groups and the centroid of the pentamethylcyclopentadienyl ring form this tetrahedron. Important bond distances are: Lu–C11: 2.56(2) Å, Lu–C12: 2.39(2) Å, Lu–C13: 2.59(2) Å, Lu–(C1 to C5)$_{(ave)}$: 2.70(2) Å.

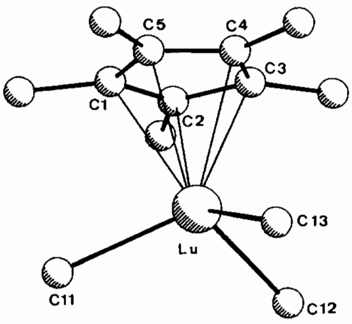


Fig. 2. PLUTO drawing of the anion in $[Li(tmed)_2][C_5Me_5Lu(CH_3)_3]$.

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