

Synthesis and Characterization of Lanthanide Complexes Involving Silylene-Bridged Fluorenyl

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By the reaction of bis-(9-fluorenyl)(methyl)(phenyl)-silylene lithium with LnCl_3 ($\text{Ln} = \text{Yb, Dy, Pr, La, Sm, Nd}$), six new lanthanide complexes were synthesized. All the complexes were characterized by elemental analysis, infrared spectra and mass spectra.

Key Words: Rare earth trichloride, Bis-(9-fluorenyl) (methyl)(phenyl)-silylene lithium, Synthesis.

INTRODUCTION

Although fluorenyl rare earth organometallic complexes were synthesized by Kalsotra in 1972, until 1994 the crystal of fluorenyl rare earth organometallic complexes was reported by Evans *et al.*¹ Even though the fluorenyl rare earth organometallic complexes very difficult to synthesize, the silylene-bridged fluorenyl rare earth organometallic complexes had been applied in the catalytic field².

Silylene-bridged fluorenyl has a relative stability. The organometallic complexes of alkali metals, alkaline earth metals³ and group-IV metal ions⁴ have been reported in recent years, but similar rare earth organometallic complexes have been reported very little. Qian *et al.*⁵ and Hermann *et al.*⁶ had synthesized $[\text{Me}_2\text{Si}(\text{FulCpYCl})]_2^5$ and $\text{Me}_2\text{Si}(\text{Ind}_2\text{YN}(\text{SiHMe}_2)_2)_2^6$ respectively through salt eliminating reaction and amine eliminating reaction. In this experiment, we have synthesized the organometallic complexes through the reaction of bis-(9-fluorenyl)(methyl)(phenyl)-silane lithium with LnCl_3 .

EXPERIMENTAL

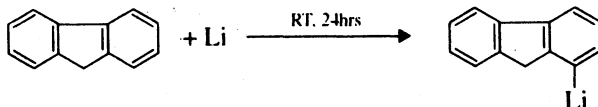
Synthesis of the lanthanide complexes was carried out under purified argon atmosphere using Schlenk techniques. THF and n-hexane were refluxed and distilled over the sodium ketyl of benzophenone under argon atmosphere immediately before use. The decomposition temperature of the complexes was determined in argon-filled sealed capillaries and uncorrected. The analysis for C, H was obtained on Yanaco MT-2 analyzer. The analytical results for Ln were obtained by the known method⁷. IR spectra were recorded on a Mattson Alpha Centauri FT-IR spectrophotometer (KBr crystal plate). Mass spectra were re-

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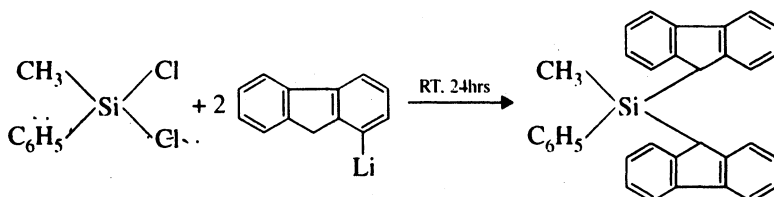
corded on a HP 5989A mass spectrometer. Rare earth trichloride were prepared by the literature methods.⁸

Preparation of fluorenyl lithium.



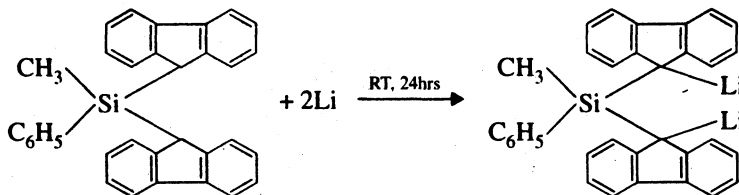
10 g (60 mmol) of dry fluorene and 2 g (289 mmol) of lithium were added under water-free and oxygen-free condition in a dry 100 mL Schlenk flask. They were dissolved in 100 mL of dry THF. The yellow mixture was stirred for 48 h, to get fluorenyl lithium.

Preparation of Bis-(9-fluorenyl)(methyl)(phenyl)silylene.



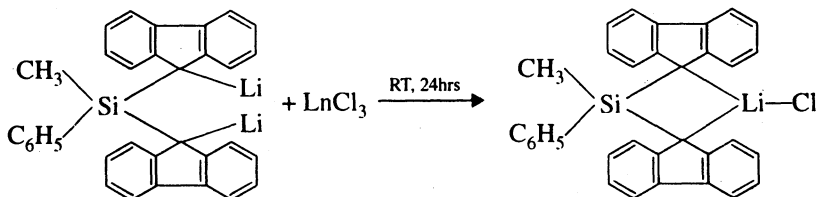
Dichlorine(methyl)(phenyl)silane (4.9 mL, 30 mmol) was added dropwise at room temperature to the flask containing a THF solution of fluorenyllithium. The reaction mixture was stirred for an additional 24 h. The solvent was removed under vacuum and the residue was treated with 30 mL of n-hexane, the crude product was washed by n-hexane to afford a white solid. m.p. 208–212°C. C₃₃H₂₆Si, found (calcd., %): C: 88.02 (88.00); H: 5.79 (5.78). ¹H NMR (500 MHz, CDCl₃, 27°C), δ (ppm) = 7.71–7.77 (d, 6H, aromH), 7.30–7.33 (t, 8H, aromH), 7.15–7.18 (t, 2H, aromH), 7.09–7.10 (t, 1H, aromH), 6.85–6.88 (t, 2H, aromH), 6.49–6.51 (t, 2H, aromH), 4.64 (s, 2H, H-9, Flu), –0.32 (s, 3H, CH₃), ¹³C NMR, –10.001, 39.623, 120.109, 120.186, 124.603, 125.700, 125.750, 126.262, 126.295, 126.773, 129.266, 134.076, 141.044, 141.159, 144.397, 144.440. MS: m/z 450 (M⁺, 4.66%).

Preparation of (CH₃)(C₆H₅)Si(C₁₃H₉)₂Li₂



A certain amount of (CH₃)(C₆H₅)Si(C₁₃H₉)₂ and 2 g (389 mmol) of lithium were added under oxygen-free condition in a dry 100 mL of dry THF. The yellow mixture was stirred for 48 h, to receive the desired product.

Preparation of $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Si}(\text{C}_{13}\text{H}_8)_2\text{LnCl}$



To a suspension of LnCl_3 in 50 mL THF, $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Si}(\text{C}_{13}\text{H}_8)_2\text{Li}_2$ was added dropwise at about 0°C to -5°C . The resulting suspension was allowed to warm to ambient temperature and stirred overnight under argon. The precipitate was separated by centrifugation and the clear solution was concentrated. The residue was extracted with THF after vacuum distillation and the solid was obtained.

RESULTS AND DISCUSSION

Complexes I–VI have been characterized by elemental analysis (C, H and Ln), IR and mass spectra. The physical properties and elemental analysis are listed in Table-1.

TABLE-1
PHYSICAL PROPERTIES AND THE ELEMENTAL ANALYSIS DATA FOR
COMPLEXES I-VI

Complexes (Color)	Decomposition ($^\circ\text{C}$)	Yield (%)	Elemental analysis % found (calcd.)		
			Ln	C	H
I (Yb) (White)	140	72	25.98 (26.33)	59.97 (60.27)	3.43 (3.65)
II (Dy) (White)	118	80	25.19 (25.33)	60.87 (61.16)	3.48 (3.71)
III (Pr) (Yellow)	138	75	21.98 (22.60)	63.13 (63.46)	3.67 (3.85)
IV (La) (Yellow)	141	83	21.86 (22.35)	63.24 (63.66)	3.53 (3.86)
V (Sm) (Yellow)	142	90	23.59 (23.68)	61.95 (62.51)	3.32 (3.79)
VI (Nd) (Yellow)	137	86	22.31 (22.95)	62.87 (63.11)	3.64 (3.83)

The elemental analyses for all the complexes are in agreement with the general formula $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Si}(\text{C}_{13}\text{H}_8)_2\text{LnCl}$.

The IR spectral data for complexes I to VI are shown in Table-2. all the six complexes exhibit methyl, phenyl and Ln—Cl bond absorption at 2900–2800, 1600–1400, 440–410 cm^{-1} ; the last one is tentatively assigned to the characteristic absorption of δ -bonded group when bound to rare earth metal. The mass spectra of these complexes are given in Table-3.

TABLE-2
IR SPECTRA DATA (cm⁻¹) FOR COMPLEXES I-VI

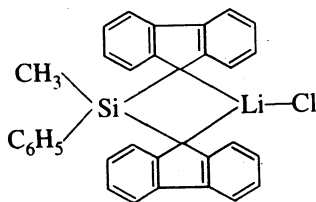
Complexes	Main peaks
(I) Yb	2962, 2925, 2835, 1632, 1457, 1428, 1261, 790, 737, 403, 390
(II) Dy	3069, 2961, 2924, 2851, 1634, 1476, 1428, 1260, 1098, 1028, 872, 798, 1098, 1028, 872, 798, 437
(III) Pr	3066, 3047, 2956, 2923, 2852, 1646, 1615, 1516, 1448, 1427, 1114, 1020, 983, 738, 484, 442
(IV) La	3065, 3046, 2952, 2923, 2851, 1611, 1601, 1505, 1476, 1115, 984, 781, 738, 484, 456
(V) Sm	3068, 2962, 1635, 1475, 1446, 1260, 1098, 1027, 790, 484, 443
(VI) Nd	3067, 2961, 2933, 1634, 1476, 1260, 1049, 1028, 789, 737, 481, 430

TABLE-3
MS DATA FOR THE COMPLEXES I ~ VI

Complexes	Main Peaks
(I) Yb	657 (M ⁺ , 1.90%), 621.5 (M ⁺ -Cl, 1.2%), 448 (M-Yb-Cl), 330 (2C ₁₃ H ₉ ⁺ , 8.41%), 208.5 (Yb-Cl, 0.17%), 173 (Yb, 1.72%), 165 (^o C ₁₃ H ₉ , 87.4%), 77 (^o C ₆ H ₅ , 15.68%).
(II) Dy	647.5 (M ⁺ , 2.3%), 612 (M ⁺ -Cl, 3.5%), 448 (M-Dy-Cl, 0.18%), 330 (2C ₁₃ H ₉ ⁺ , 3.84%), 165 (^o C ₁₃ H ₉ , 100%), 164 (Dy, 1.36%), 199 (Dy-Cl, 2.20%), 77 (^o C ₆ H ₅ , 34.29%).
(III) Pr	624 (M ⁺ , 4.0%), 589 (M ⁺ Cl, 4.0%), 447 (M-Pr-Cl, 3.2%), 330 (2C ₁₃ H ₉ ⁺ , 22.05%), 165 (^o C ₁₃ H ₉ , 65.89%), 141 (Pr, 1.76%), 177 (Pr-Cl, 2.55%), 77 (^o C ₆ H ₅ , 4.15%).
(IV) La	622 (M ⁺ , 0.12%), 586.5 (M ⁺ -Cl), 448 (M-La-Cl, 6.96%), 165 (^o C ₁₃ H ₉ , 100%), 330 (2C ₁₃ H ₉ ⁺ , 9.93%), 174 (La-Cl, 6.96%), 165 (^o C ₁₃ H ₉ , 100%), 138.9 (La, 15.26%), 77 (^o C ₆ H ₅ , 14.32%).
(V) Sm	633.5 (M ⁺ , 16.63%), 598 (M ⁺ -Cl, 2.49%), 483 (M-Sm-Cl, 2.32%), 330 (2C ₁₃ H ₉ ⁺ , 19.53%), 165 (^o C ₁₃ H ₉ , 60.48%), 150 (Sm, 9.88%), 77 (^o C ₆ H ₅ , 1.99%).
(VI) Nd	627.5 (M ⁺ , 0.43%), 592 (M-Cl, 0.44%), 330 (2C ₁₃ H ₉ ⁺ , 33.05%), 165 (^o C ₁₃ H ₉ , 80.31%), 144 (Nd, 2.32%), 179.5 (Nd-Cl, 9.65%), 77 (^o C ₆ H ₅ , 4.16%).

It can be seen from Table-3 that molecular ion peaks of the complexes I-VI and some other regular related fragment ion peaks are obtained. All the complexes have Ph, C₁₃H₉, Ln fragment ion peaks. So we suppose the main fragmentation of the complexes as follows:

From the above discussion, the proposed structure for these title complexes is:



Ln = Yb, Dy, Pr, La, Sm, Nd

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