*Asian Journal of Chemistry* Vol. 14, No. 3–4 (2002), 1463–1468

# Synthesis and Characterization of Rare Earth Complexes Containing Piperonal Dimethyl Acetal and Dicyclopentadienyl

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Five new organolanthanide complexes $C_{20}H_{21}O_4Ln$ (Ln : Yb, Dy, Pr, La, Sm) was synthesized by the reaction of anhydrous $Cp_2InCl$ with $LiC_{10}H_{11}O_4$ in THF at low temperature, these complexes were characterized by elemental analysis, IR and MS.

**Key Words: Rare earth, 6-Bromopipernal dimethyl acetal, Dicyclopentadienyl rare earth chlorine.**

## INTRODUCTION

Because of the unique structural characterization and catalytic property of cyclopentadienyl rare earth organometallic complexes, it occupies an important position in rare earth organometallic chemistry. In order to get cyclopentadienyl rare earth organometallic complexes, it mostly uses anhydrous rare earth trichloride as starting material, reacting with cyclopentadienyl sodium or cyclopentadienyl potassium. In recent years, the synthesis and characterization of naphthyl rare earth organometallic complexes have been reported,[1,2] but the piperonal dimethyl acetal has not yet been reported. Ligand 6-bromopiperonal dimethyl acetal is an intermediate of synthesizing podophylloxin, is a natural anticancer medicine. In this experiment, we used piperonal as raw material, made it become a stable 6-bromopiperonaldimethylacetal, and cultivated the single crystal seen in Fig. 1. In order to inquire into the synthetic method of rare earth organometallic complexes, we used ligand reacting with lithium; the resulting product reacts again with dicyclopentadienyl rare earth chloride to yield five new rare earth organometallic complexes containing Ln—C bond.

## EXPERIMENTAL

The synthesis of these lanthanide complexes was carried out under purified argon using Schlenk techniques. THF and n-hexane were refluxed and distilled over the sodium ketyl of benzophenone under argon immediately before use. The

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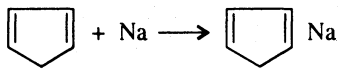
decomposition temperatures of the complexes were determined in argon-filled sealed capillaries. C and H were performed on Yanaco MT-2 analyzer. Ln was analyzed by known method. A MS spectrum was recorded on a HP 5989A spectrometer. Rare earth trichloride cyclopentadienyl sodium, 6-bromo-pipernal dimethyl acetal dicyclopentadienyl rare earth chloride were prepared by the literature methods[4-11].

**Synthesis routes:**

(1)

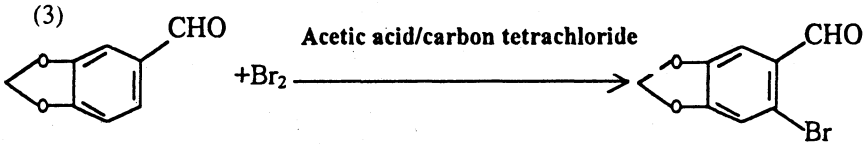



. . . (1)

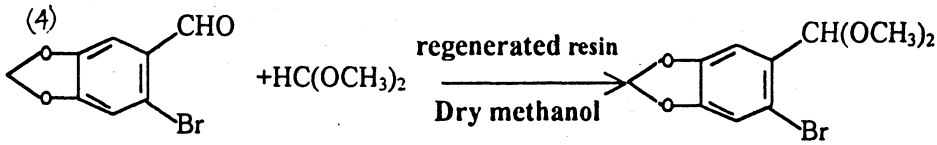
(2) $LnCl_3 + 2CpNa \longrightarrow Cp_2InCl + 2NaCl$ . . . (2)

| Complexes | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Ln | Yb | Dy | Pr | La | Sm |

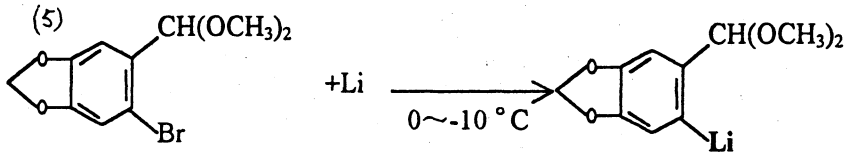
(3)



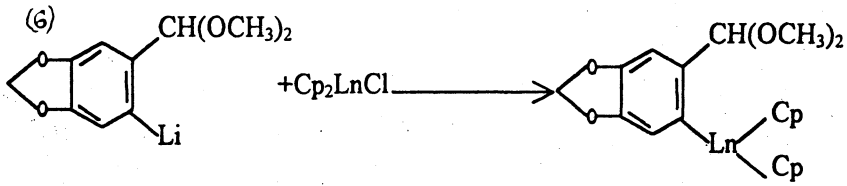

(4)




(5)




(6)




**Preparation of 6-bromopiperonal:** A 500 mL round-bottom flask, equipped with a pressure equalising dropping funnel, was charged with a solution of piperonal (20.1 g, 0.134 mol) in 140 mL of acetic acid/carbon tetrachloride (10/1) and a catalytic amount of iodine. The dropping funnel was charged with a solution

of bromine (20 mL, 57.2 g, 0.358 mol, and 2.7 eq) in 140 mL of acetic acid/carbon tetrachloride (10/1) and this was added dropwise to the flask while stirring. Once addition was completed, the mixture was poured into one litre of cold water to give an orange precipitate. Potassium metabisulphite (10 g, 45 mmol) was added while stirring to remove with water Two crystallizations with toluene afforded 18.7 g of 6-bromo-piperonal as white needles (82 mmol, 61% yield). m.p. 129–130°C; $^1$H NMR (500 MHz): 6.1 (s, 2H, —$OCH_2O$—), 7.0 (s, 1H, aromatic), 7.3 (s, 1H, aromatic) and 10.2 (s, 1H, CHO); (KBr) $\nu_{max}$: 1690 $cm^{-1}$ strong (CHO), see routes 3.

**Preparation of 6-bromopiperonal dimethyl acetal:** In the presence of a catalytic amount of regenerated resin, 10 g of dry 6-bromopiperonal (44 mmol) was dissolved in 100 mL of dry methanol in a dry 250 mL round-bottom flask equipped with an efficient magnetic stirrer and a condenser topped with a $CaCl_2$ tube; then 8 mL of trimethyl orthoformate was added and the methanol was brought to the boil. After 24 h at room temperature the solvent was evaporated in vacuum using a rotary evaporator to yield 13.2 g of a green-brown oil. Vacuum distillation afforded the title compound as 11.5 g of a colorless liquid in 95% yield; b.p. = 118X (0.2 mbar); δ H (500 MHz): 3.4 (s, 6H, CH $(OMe)_2$), 5.5 (s, 1H, CH $(OMe)_2$), 6.0 (s, 2H, —$OCH_2O$—), 7.0 (s, 1H, aromatic) and 7.1 (s, 1H, aromatic); m.p. around 20X; see routes 4 and Fig. 1.

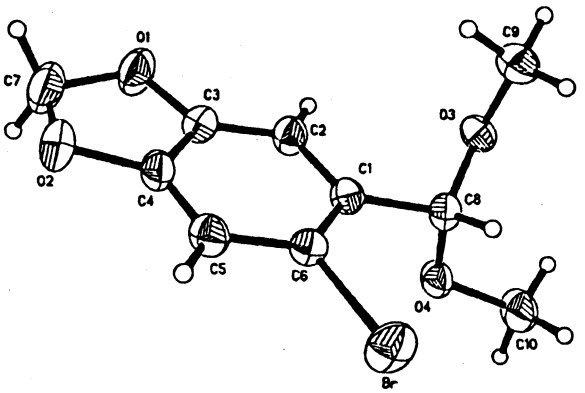



Fig. 1. The crystal structure of 6-bromopipernal dimethyl acetal

**Preparation of piperonal dimethyl acetal lithium:** 2 g (289 mmol) of lithium and 1 g (3.60 mmol) of 6-bromopiperonal dimethyl acetal were diluted with 30 mL dry THF under argon in a 100 mL Schlenk flask. The stirred solution was cooled down to 0 to –5X. The resulting green solution was stirred for 48 h to get the desired compound; see routes 5.

**Preparation of dicyclopentadienyl rare earth chloride:** A known amount of anhydrous $LnCl_3$ was diluted with 30 mL of dry THF under argon in a 100 mL Schlenk flask and a ration of cyclopentadienyl sodium was added dropwise. The resulting yellow mixture was stirred for 48 h to get the desired compound; see routes 2.

**Preparation of rare earth organometallic complexes:** A solution of

dicyclopentadienyl rare earth chloride 4 was cooled down to 0 to −5°C and $C_{10}H_{11}O_4Li$ was added dropwise under the atmosphere of argon. The resulting yellow mixture was stirred for 48 h and then was allowed to warm up to room temperature. The resulting solution was concentrated in vacuum to about 20 mL. By addition of 30 mL of n-hexane, a solid precipitated out which was recrystallized in THF/n-hexane. It was washed twice with THF/n-hexane and dried in vacuum; see routes 6.

The other complexes were synthesized by the same method.

## RESULTS AND DISCUSSION

Complexes I to V were characterized by elemental analysis (C, H and Ln), IR and mass spectra. The physical properties and results of elemental analysis are listed in Table-1. The result of elemental analysis for all the complexes is in agreement with the general formula $C_{20}H_{21}O_4Ln$.

TABLE-1
PHYSICO-CHEMICAL DATA OR COMPLEXES I–V

| Complexes (Colour) | m.p. (X) | Yield (%) | % Analysis, Found (Calcd) | | |
|---|---|---|---|---|---|
| | | | Ln | C | H |
| **(I)** Yb (Yellow) | > 300 | 40 | 33.91 (34.70) | 47.23 (48.09) | 3.92 (4.01) |
| **(II)** Dy (Dark) | > 300 | 70 | 32.81 (33.09) | 45.72 (46.08) | 4.08 (4.29) |
| **(III)** Pr (White) | > 300 | 65 | 29.78 (30.25) | 50.49 (51.51) | 4.38 (4.51) |
| **(IV)** La (Red) | > 300 | 60 | 29.23 (29.99) | 50.68 (51.72) | 4.27 (4.55) |
| **(V)** Sm (Yellow) | > 300 | 72 | 30.92 (31.44) | 49.97 (50.31) | 4.18 (4.40) |

The IR spectral data for complexes **I** to **V** are shown in Table-2. All the five complexes exhibit characteristic absorption 2960, 2925, 1503, 1461, 1025, 780, 440 $cm^{-1}$. The last one is tentatively assigned to the characteristic absorption of π-bonded cyclopentadienyl group when bound to rare earth metals.

TABLE-2
IR DATA ($cm^{-1}$) OF COMPLEXES I–V

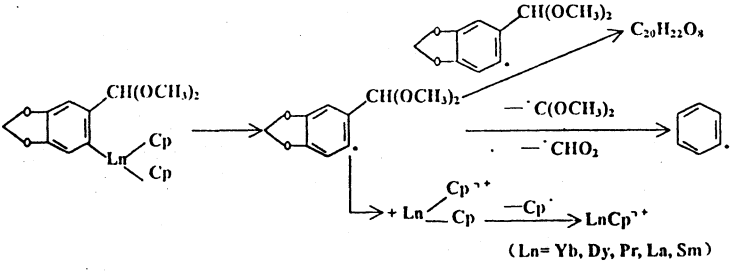
| Complexes | Main Peaks |
|---|---|
| **(I)** Yb | 2963, 2925, 1731, 1644, 1503, 1477, 1407, 1012, 778, 440 |
| **(II)** Dy | 2954, 2902, 2833, 1734, 1502, 1480, 1411, 1041, 791, 437 |
| **(III)** Pr | 2960, 2934, 2902, 2829, 1728, 1632, 1503, 1482, 1040, 801, 443 |
| **(IV)** La | 2955, 2925, 2854, 1728, 1631, 1503, 1478, 1410, 1040, 797, 442 |
| **(V)** Sm | 2957, 2929, 2898, 1728, 1632, 1503, 1444, 1040, 794, 446 |

The mass spectra of these complexes are given in Table-3. From these, the molecular ion peaks of the complexes **I–V** and some other regular related fragment ion peaks are obtained.

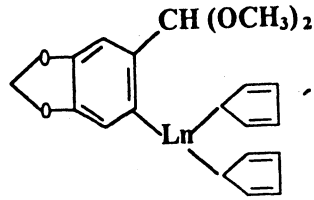
TABLE-3
MS DATA OF COMPLEXES **I–V**

| Complexes | Main Peaks |
|---|---|
| (I) Yb | 499 [$(C_{20}H_{21}O_4Yb)^+$, 0.23%], $C_{20}H_{22}O_8$ (3.03%), Yb-$C_{10}H_{11}O_4$ (6.92%), $Cp_2Yb$ (1.24%), CpYb (15.73%), $C_7H_6O_2^{\bullet}$(31.15%), $^{\bullet}C(OCH_3)_2$ (18.00%), $^{\bullet}C_6H_5$(38.04%) Cp $^{\bullet}$(36.05%), CpH (100%), $^{\bullet}CHO_2$ (17.9%). |
| (II) Dy | 489 [$(C_{20}H_{21}O_4Dy)^+$, 0.57%], $C_{20}H_{22}O_8$(5.73%), Dy-$C_{10}H_{11}O_4$ (2.28%), CpDy (2.08%), $C_{10}H_{11}O_4$ (2.82%), $Cp_2Dy$ (12.02%), $^{\bullet}C_6H_5$ (9.55%), $C_7H_6O_2^{\bullet}$ (1.01%)$Cp^{\bullet}$ (5.74%) $^{\bullet}C(OCH_3)_2$ (15.92%), $^{\bullet}CHO_2$ (100%) |
| (III) Pr | 466 [$(C_{20}H_{21}O_4Pr)^+$, 0.82%], $C_{20}H_{22}O_8$ (1.34%), $Cp_2Pr$ (5.51%), CpPr (3.93%), Pr-$C_{10}H_{11}O_4$ (3.68%), $C_{10}H_{11}O_4$ (2.54%), $^{\bullet}C(OCH_3)_2$ (0.97%), CpH (100%), $Cp^{\bullet}$ (0.95%), $^{\bullet}C_6H_5$ (0.91%), $C_7H_6O_2$ (2.95%), $^{\bullet}CHO_2$ (21.2%). |
| (IV) La | 464 [$(C_{20}H_{21}O_4La)^+$, 0.08%], $C_{20}H_{22}O_8$ (10.11%), $Cp_2La$ (10.73%), La-$C_{10}H_{11}O_4$ (0.72%), $C_{10}H_{11}O_4$ (0.6%), $^{\bullet}C(OCH_3)_2$ (8.76%), $^{\bullet}C_6H_5$ (16.77%), CpH (100%), $^{\bullet}CHO_2$(25.6%). |
| (V) Sm | 477 [$(C_{20}H_{21}O_4Sm)^+$, 0.15%], $C_{20}H_{22}O_8$ (0.15%), Sm-$C_{10}H_{11}O_4$ (0.87%) $C_{10}H_{11}O_4$ (0.9%), $Cp_2Sm$ (10.32%), CpSm (0.41%), $^{\bullet}C_6H_5$ (7.49%), CpH (100%), $Cp^{\bullet}$ (28.46%), $^{\bullet}C(OCH_3)_2$ (15.77%), $C_7H_6O_2$ (2.76%), $^{\bullet}CHO_2$ (15.21%). |

According to the fragment ion peaks, we suppose the mechanism of their fragments are as follows:



In addition, there is no mass of fragment ion larger than that of the molecular ion; it indicates no dimer for the complexes was formed.




(Ln = Yb, Dy, Pr, La or Sm)

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

## REFERENCES

1. V. Andrey, and Lev Protchenko, *J. Organomet. Chem*, **497**, 209 (1993).
2. I.L. Fedushkin. M.N. Bochkarev, H. Schumann and L. Esser, *J. Organomet. Chem.*, **489**, 145 (1995).
3. C.T. Qian, C.Q. Ye and H. Lu, *J. Organomet. Chem.*, **247**, 161 (1983).
4. M.D. Taylor and C.P. Cartar, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962).
5. G. Wilkinson and J.M. Birminbhm, *J. Am. Chem. Soc.*, **76**, 6210 (1954).
6. B.A. Keay, *Can. J. Chem.*, **61**, 1987 (1983).
7. R. Rodrigo, *Tetrahedron*, **44**, 2093 (1988).
8. S.P. Khanepere, *J. Org. Chem.* **55**, 1471 (1990).
9. Steven P. Forsey, *J. Org. Chem.*, **54**, 4280 (1989).
10. B.A. Keay, *Can. J. Chem.*, **61** (1987).
11. R.E. Magin, S. Manastyskyj and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 672 (1963).

(*Received:* 4 March 2000; *Accepted:* 15 May 2002) AJC-2710