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Preliminary communication

THIENYL AND PERFLUOROPHENYL DERIVATIVES OF DIVALENT LANTHANIDES

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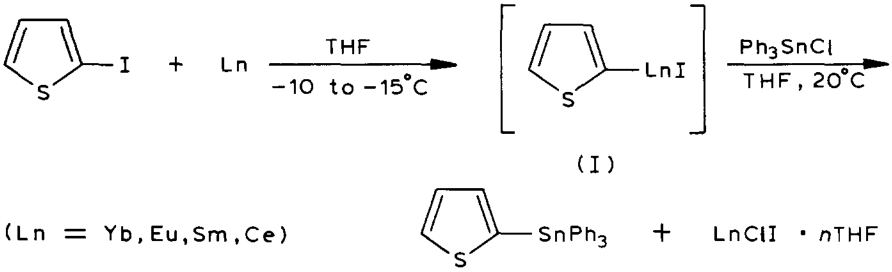
Summary

The reaction of oxidative addition of α-iodothiophene and bromopentafluorobenzene to zero-valent lanthanides has been carried out. The formation of organolanthanide derivatives RLnX (R = α-C_4H_3S, C_6F_5) has been confirmed by isolation of the corresponding $RSnPh_3$ resulting from the interaction of RLnX with Ph_3SnCl. The reaction of lanthanide with C_6F_5Br is sensitive to the nature of the metal.

This study is a continuation of our investigation of the lanthanide derivatives RLnX [1,2] (R = Me, Ph, C_6F_5). We now report the reaction of Ln with α-iodothiophene. In the presence of a promotor (CH_2I_2 [1]) the oxidative addition of metallic Ln (Yb, Eu, Sm, Ce) to α-iodothiophene proceeded easily and produced the corresponding organolanthanide compounds, which afforded thienyltriphenyltin in high yield (ca. 70%) when treated with Ph_3SnCl.



Compounds I are the first examples of heteroaromatic derivatives of lanthanides. It is noteworthy that the reaction of Ln with iodothiophene has an inductive period which is longer than that of the reaction with iodobenzene.

In the case of Ln = Sm, the inductive period is 1.5 h even in the presence of CH_2I_2. The reaction of α-iodothiophene with Ce proceeds at room temperature and is completed in 4 h (40 min in the case of iodobenzene [1]).

In a previous study of the reaction of bromopentafluorobenzene with Yb [2], it was shown that even aryl bromides are able to interact with lanthanides in the presence of electron-accepting groups in the aromatic ring.

We have also carried out this reaction with other lanthanides capable of forming divalent derivatives. The product yield, i.e. the quantity of the organolanthanide formed was found to decrease in the following order: Yb (85%), Sm (50%), Eu (20%). Cerium does not participate in the reaction. The results are given in Table 1.

TABLE 1

REACTIONS OF ARYL HALIDES (ArX) WITH LANTHANIDES METALS (Ln) IN THF

	Ln (mg-atom)		ArX (mg-atom)	Induction period (min)	Yield (%)
			α-IC₄H₃S		
1.	Yb	3.73	3.37	5	68
2.	Eu	1.79	1.70	10	67
3.	Sm	1.26	1.20	90	67
4.	Ce	2.60	2.48	40	66
			C₆F₅Br		
5.	Yb	6.11	5.55	5	85
6.	Eu	2.63	2.36	30	20
7.	Sm	1.89	1.70	60	50
8.	Ce	2.17	1.96	—	—

$$\begin{tikzcd} & & C_6F_5SnPh_3 + LnClBr\cdot n\text{THF} \\ C_6F_5Br + Ln \arrow[r, "\text{THF}", "-10\text{ to }-15^\circ\text{C}"'] & {[C_6F_5LnBr]} \arrow[ur, "Ph_3SnCl"] \arrow[dr, "H_2O"'] & \\ & & C_6F_5H + LnBrOH\cdot n\text{THF} \end{tikzcd} \quad (2)$$

In the same way, the lanthanide derivatives C_6F_5LnX, including one of Ce, may be prepared from the corresponding PhLnI compound (Ln = Yb, Eu, Ce) and pentafluorobenzene.

$$PhLnI + C_6F_5H \xrightarrow[1\text{—}1.5\text{ h}]{\text{THF, }20^\circ\text{C}} [C_6F_5LnI] + PhH \xrightarrow[20^\circ\text{C}]{Ph_3SnCl}$$

$$C_6F_5SnPh_3 + LnClI\cdot n\text{THF}$$

The reaction has been shown to be completed in 1—1.5 h (based on the yield of the organotin compound).

Experimental

Metallic lanthanides (Yb, Eu, Sm, Ce, as small chips and 99% purity by distillation) were used. All the syntheses of the organolanthanide compounds and their treatment were carried out under dry argon. THF was purified by refluxing it with Na/benzophenone and was distilled immediately before the reaction. The reaction was followed by thin-layer chromatography (TLC) on the "Silufol UV-254" plates developed by UV light. The constants of α-iodothiophene, bromopentafluorobenzene and Ph_3SnCl are in agreement with literature data.

Reactions of α-iodothiophene with metallic lanthanides. A solution of α-iodothiophene in 15 ml of THF was added dropwise to the metallic lanthanide activated by CH_2I_2 in 10 ml of THF at −10 to −15°C. To complete the reaction, the mixture was stirred at this temperature for 4 h (the end of the reaction was determined by disappearance of the initial α-iodothiophene with TLC). Then the temperature of the reaction mixture was increased to +10°C and the solution of α-thienyllanthanide iodide was used in situ in further reactions.

Solutions of C_6F_5LnBr (Ln = Yb, Eu, Sm, Ce) were prepared by analogous procedures.

Reactions of perfluoroaryl- and heteroaryl-lanthanides with Ph_3SnCl. A solution of ArLnX, obtained as described above, was treated with a solution of Ph_3SnCl in THF at +10°C. To complete the reaction, the mixture was allowed to warm slowly to 25°C. After hydrolysis of the reaction mixture with water acidified with HCl, the organic layer was separated. The water layer was extracted by ether; the combined ether extracts were dried over anhydrous Na_2SO_4. After removal of ether, Ph_3SnAr was isolated in ca. 70% yield.

References

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