Variation of luminescence properties of the reaction solution during preparation of a component of Ziegler—Natta catalyst by the reaction of Tb with Ph_3CCl

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Photoluminescence is used to test lanthanide—C bonds and to identify unstable intermediates in the synthesis of Ph_3CTbCl_2, a component of Ziegler—Natta catalyst.

Key words: lanthanides, photoluminescence, catalyst.

Luminescence of organolanthanide compounds (OLC) is the least known among luminescent properties of lanthanide compounds.[1—3] Some OLC, in combination with alkylaluminum, are important components of a number[5] of Ziegler—Natta type[4] catalytic systems. Previously we showed that the measurement of photoluminescence (PL) and chemiluminescence (CL) of these systems can provide valuable information concerning the processes of preparation of the catalysts and the mechanism of their action.[5]

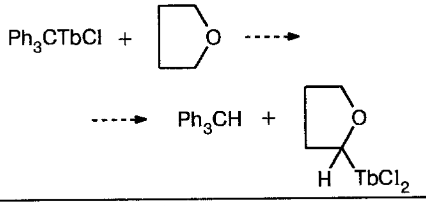
In the present work we studied the variation of the spectra of PL excited by UV radiation in one of the transparent bends of a reactor during the synthesis of a lanthanide complex, a component of the known[6] catalyst of polymerization of dienes, by the reaction of Tb metal with Ph_3CCl in THF in a nitrogen atmosphere or *in vacuo* (under conditions in which only Ph_3CTbCl_2 is formed in the solution and no analogous monochloride complex is produced).

Some time after mixing the reactants the intensity of the PL band of Ph_3CCl (λ_{max} = 440 nm) decreases (Fig. 1, curve *1*), and PL bands (λ_{max} = 524 and 553 nm) corresponding to the reaction intermediate, trityl radical (TR), appear (curve *2*).

$$Ph_3CCl + Tb \dashrightarrow Ph_3CTbCl \qquad (1)$$

$$Ph_3CTbCl + Ph_3CCl \dashrightarrow Ph_3CTbCl_2 + Ph_3C^{\cdot} \qquad (2)$$

$$2Ph_3C^{\cdot} \leftrightarrows Ph_3C{-}CPh_3 \qquad (3)$$



(4)

Previously[6] the formation of TR in reactions (1, 2) has been postulated based on the results of chemical analysis of stable products of the reaction of Tb with

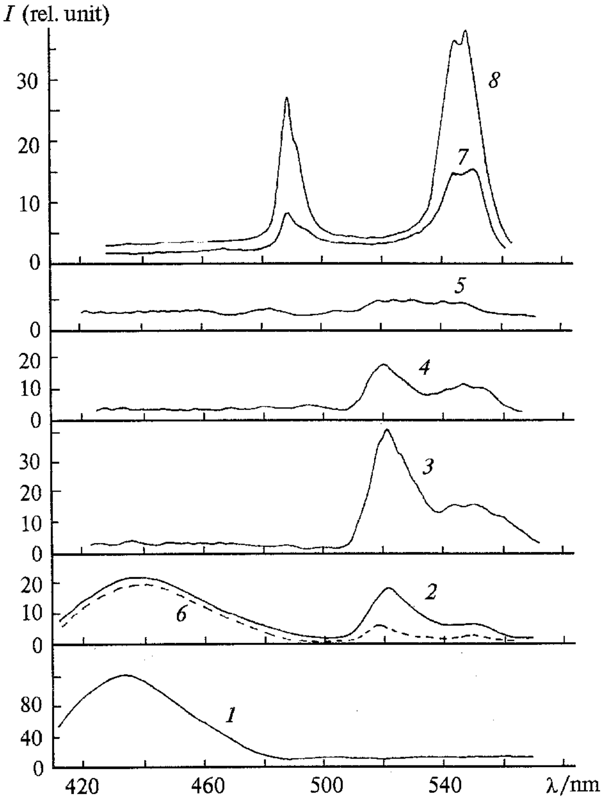


Fig. 1. Variation of the PL spectrum of the reaction solution during reaction of Tb(O) with Ph_3CCl in THF as a function of the duration of stirring: the starting solution: Ph_3CCl ($8.5 \cdot 10^{-2}$ mol L^{-1}) in THF (5 mL) + Tb ($6.7 \cdot 10^{-4}$ mol) (*1*); after 5 min (*2*); 30 min (*3*); 1 h (*4*); 2 h (*5*); 24 h (*6*); 7 days (*7*); 10 days (*8*); λ_{exit} = 365 nm, *1—5*, 300 K, *6—8*, 77 K.

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Ph_3CCl. The PL spectra of this radical at 300 K and 77 K correlate well with the PL spectra of the TR obtained previously in other reactions.[7,8] The recording of the PL of TR is the first direct evidence for its formation in this system. The complete disappearance of the PL of Ph_3CCl and TR (curve *5*) is caused by its quenching by Ph_3C^- anion incorporated in the Ph_3CTbCl_2 complex, rather than by the entire consumption of these species.

In fact, when the reactor is cooled to 77 K, the disappeared PL of Ph_3CCl and TR is again recorded (curve *6*). The maxima of PL bands of TR shift to the short-wave region (λ_{max} = 517, 545 nm). After disappearance of the PL of Ph_3CCl and TR at 300 K, the solution turns red, due to the formation of Ph_3C^-. However, PL of Ph_3CTbCl_2 is not recorded, since luminescence of Tb^{3+} is quenched by Ph_3C^- anion. The characteristic PL of Tb^{3+} (λ_{max} = 490 and 544, 552 nm, corresponding to $^5D_4$—$^7F_6$ and $^5D_4$—$^7F_5$ transitions) appears, when Ph_3CTbCl_2 is converted to another OLC, the product of metallation of THF according to reaction (4) (see Fig. 1, curves *7*, *8*). Since in this system, an OLC of terbium with THF may be formed only by reaction (4), the existence of PL of Tb^{3+} indicates formation of a Ln—C bond in the Ph_3CTbCl_2 complex. This is also indicated by the CL detected by us in the reaction of Ph_3CTbCl_2 (see Ref. 9). Previously, the formation of a Ln—C bond in this system was judged by the red color typical of Ph_3C^- and the data of chemical analysis.[5]

Thus, the PL and CL methods are promising for testing Ln—C bonds and for identification of unstable intermediates in the synthesis of components of Ziegler—Natta catalysts.

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Electrochemical reduction of phenylethynyl halides and related compounds

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Reduction of phenylethynyl halides PhC≡CHal (Hal = I (**1**), Br (**2**), Cl (**3**)), diiodoacetylene (**4**), (phenylethynyl)triphenylphosphonium bromide (**5**), and related compounds in THF was studied by means of cyclic voltammetry using a glassy-carbon electrode. Compounds **1**—**5** are reduced with cleavage of the C—Hal bond, and the reduction potentials increase in the order **3** < **2** < **1** < **4** < **5**.

Key words: electroreduction, alkynyl halides.

The reaction of metal carbonyl anions $[M]^-$ with haloacetylenes and ethynylphosphonium salts[1,2] is one of the methods for preparing σ-ethynylmetalcarbonyl compounds, [M]—σ-C≡CR. The known[3] reducing

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