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

S. M. Peregudova, L. I. Denisovich, N. A. Ustynyuk, L. I. Leont'eva, V. N. Vinogradova, and T. V. Filatova*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

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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Table 1. Reduction potentials of phenylethynyl halides and related compounds

Compound	$-E_{1/2}$*/V	n	E_a**/V
Ph—C≡C—I (**1**)	1.68	1	0.68; 0.93 (0.60; 0.92)
Ph—C≡C—Br (**2**)	2.00	1	0.97; 1.27 (0.98; 1.25)
Ph—C≡C—Cl (**3**)	2.29	2	1.13 (1.13)
I—C≡C—I (**4**)	1.60	1	0.60; 0.94
$[C_6H_5C{\equiv}CPPh_3]^+Br^-$ (**5**)	1.44	1	
Ph—C≡C—H (**6**)	2.72	2	
C_6H_5—C≡C—C≡C—C_6H_5 (**7**)	2.26	2	

Note. Reduction conditions: THF, 0.2 mol L^{-1} Bu_4NBF_4, v = 200 mV s^{-1}, $C = 2 \cdot 10^{-3}$ mol L^{-1}.

* $E_{1/2}$ corresponds to $E_{3/4}$ of a peak. ** E_a are potentials of anodic peaks observed after backward potential scanning; the potentials of anodic peaks of halide anions are given in parentheses.

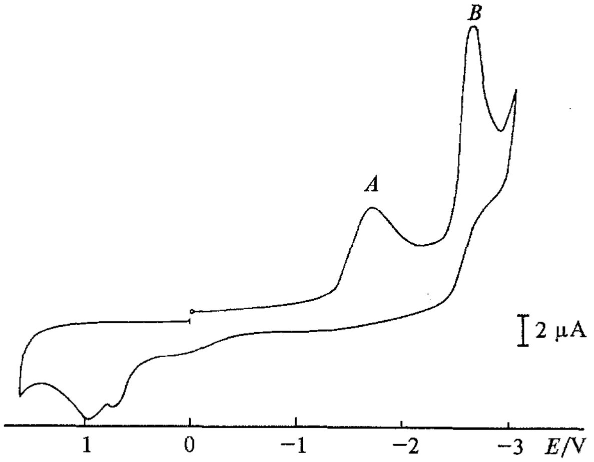
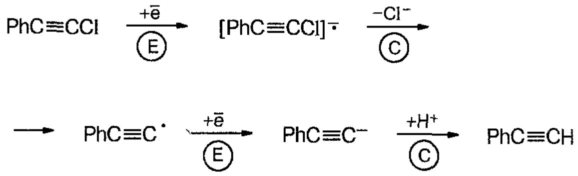


Fig. 1. Cyclic voltammogram of Ph—C≡C—I ($C = 2 \cdot 10^{-3}$ mol L^{-1}, THF, 0.2 mol L^{-1} Bu_4NBF_4, glassy-carbon cathode, 200 mV s^{-1}).

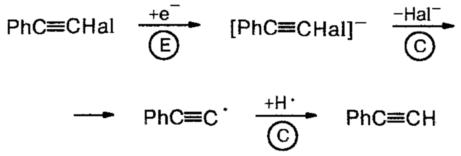
properties of $[M]^-$ suggest that this synthesis involves a step of electron transfer. This stimulated us to study the susceptibility of phenylethynyl halides and ethynylphosphonium salts to reduction using cyclic voltammetry (Table 1). The reduction was carried out in THF at a glassy-carbon electrode, since we found that compounds **1** and **2** cannot be studied at a mercury electrode, because they react with mercury. Therefore, the published data[4] on electrochemical reduction of compound **4** at a mercury electrode require verification. No data concerning electrochemical properties of phenylethynyl halides have been reported, except for the reduction potential of bromide **2**.[5]

We found that the ethynyl halides **1**—**4** studied are reduced irreversibly (Fig. 1, peak *A*) with cleavage of the C—Hal bond to give halide anions. This is indicated by the appearance of peaks on the anodic branch of the voltammogram, whose potentials (see Table 1, E_a) are close to the potentials of Hal^- measured by us under similar conditions. The numbers of electrons consumed (n) and the reduction potentials ($E_{1/2}$) of compounds **1**—**7** are presented in Table 1. From these data, it follows that the susceptibility of compounds **1**—**7** to reduction depends on the nature and number of halogen atoms in the molecule of the starting compound, as has been observed for other halogen derivatives.[6] The reduction potential of compound **4** measured by us (−1.60 V) differs from the potentials of its reduction at a mercury electrode (−0.25 V; −0.61 V),[4] which is obviously caused by interaction of compound **4** with the mercury. The irreversible peak of reduction of chloride **3** corresponds to the transfer of two electrons, whereas **1** and **2** exhibit one-electron peaks. Along with these peaks, polarograms of compounds **1**—**3** exhibit a two-electron peak *B* at a more negative potential (−2.70 V) (see Fig. 1); the potential of this peak coincides with that of the reduction peak of phenylacetylene (**6**) and differs from that of the peak of diphenyldiacetylene (**7**). The latter is reduced at substantially lower cathodic potentials (see Table 1).

Based on the data obtained, one may assume that the two-electron reduction of chloride **3** occurs according to an ECEC scheme:



According to this scheme, cleavage of the C—Cl bond in the initially produced radical anion affords PhC≡C· radical, which is reduced somewhat more readily than the starting chloride **3** (for the reduction potentials of RCl and R·, see Ref. 7) yielding PhC≡C⁻ anion. Protonation of this anion gives phenylacetylene, whose reduction peak is exhibited on voltammogram of **3**. In the case of iodide **1** and bromide **2**, the PhC≡C· intermediate radical is reduced more difficultly than **2** and, especially, than **1**. Therefore, compounds **1** and **2** undergo one-electron reduction according to an ECC scheme, and the intermediate PhC≡C· radical is stabilized by abstracting an H atom from the medium to give phenylacetylene, rather than by dimerization. In fact, the potential of peak *B* on polarograms **2** and **3** is close to that of the peak of **6**, but not **7**:



Hal = I, Br

A similar transition from two-electron reduction of a chloride to one-electron reduction in the case of bromide has been reported for 6-halo-1-phenyl-1-hexynes.[8]

As can be seen from Table 1, the peak of irreversible one-electron reduction of (phenylethynyl)triphenylphosphonium bromide **5** occurs at the lowest cathodic potential. At a more negative potential (−2.68 V), a multielectron peak occurs on the voltammogram of compound **5**; this peak is probably associated with reduction of PPh_3 (−2.60 V)[9] and PhC≡CH. These compounds may result from decomposition of the initially formed phosphonium radical:

$$[PhC{\equiv}CPPh_3]^+ \xrightarrow{+\bar{e}} [PhC{\equiv}CPPh_3]^{\cdot} \longrightarrow$$

$$\longrightarrow PPh_3 + PhC{\equiv}C^{\cdot} \xrightarrow{+H^{\cdot}} PhC{\equiv}CH$$

The results obtained can be used for elucidating the mechanism of interaction of ethynyl compounds with $[M]^-$ and other reactions involving **1—3**.

Experimental

Cyclic voltammograms were recorded using a PI-50-1 potentiostat. A glassy-carbon electrode (S = 2 mm^2) was used as the cathode, a platinum plate served as the anode, and a saturated calomel electrode was used as the reference electrode. The number of electrons (n) consumed for reduction was estimated by comparing the currents of the peaks observed with the current of the one-electron peak of the reduction of ferricinium cation under identical concentrations. THF was distilled over sodium benzophenoneketyl just before the experiments. Phenylethynyl halides **1—3** were prepared by previously published procedures.[10—12]

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