

sity ratios 1.9:1.33:1.0) are observed. Like in the case of the well-studied phthalocyanine compounds, the formation of the complex with the lutetium ion leads to a dramatic change in the long-wave region of EAS. Instead of the bands at 709 and 637 nm, bands at 672 (a) and 673 (b) nm, respectively, arose; this fact, is probably related to degeneration of the HOMO in the complex due to the change in symmetry of the ligand from  $D_{2h}$  to  $D_{4h}$ . The bands have vibrational satellites at 608 and 610 nm, respectively. The band at 515 nm undergoes a hypsochromic shift and is observed at 495 and 497 nm, respectively. The ratio of band intensities also changes significantly (2.56:1.0:0.5 (a) and 3.25:1.0:0.44 (b)). The EAS of complex (a) and those of the original metal-free compound and the previously prepared lutetium bis(octaocetylthioporphyrate)<sup>2</sup> are presented in Fig. 1. The absence of a signal in the ESR spectra (in comparison to the bis-complex, which has a signal with  $g = 2.0033$ ), and the presence of the acetate group (IR

and NMR data) along with the described synthetic route (which assists mono-complex formation) suggest the proposed formulae for the synthesized compounds.

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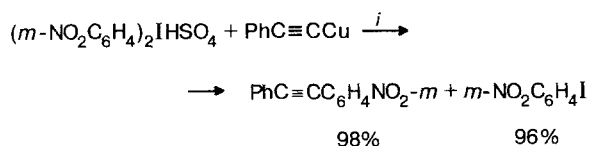
## Palladium catalyzed cross coupling of diaryliodonium salts with copper acetylide

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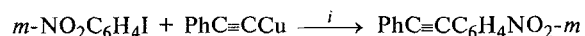
The reaction of copper acetylides with aryl halides needs rather drastic conditions (prolonged refluxing in pyridine or DMF).<sup>1,2</sup> This reaction proceeds at a high rate at ambient temperature in the presence of Pd complexes and sodium iodide in acetone.<sup>3</sup>

We found that copper phenylacetylide reacts with bis(*m*-nitrophenyl)iodonium salts in DMF or acetone in the presence of NaI and Pd complexes. It should be noted that this reaction may also be carried out in aqueous media using NaI · 2H<sub>2</sub>O. At the first stage, the reaction of copper phenylacetylide with diaryliodonium salt rapidly affords *m*-nitrotolan and *m*-iodonitrobenzene:



i. PdCl<sub>2</sub>, NaI · 2H<sub>2</sub>O, 20 °C, 15 min.

At the second stage, copper phenylacetylide reacts somewhat more slowly with *m*-iodonitrobenzene:



i. PdCl<sub>2</sub>, NaI · 2H<sub>2</sub>O, 20 °C, 1 h.

It was shown independently that copper phenylacetylide reacts quantitatively with *m*-iodonitrobenzene in the presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and NaI · 2H<sub>2</sub>O in aqueous acetone at ambient temperature within 1 h.

(*m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>IOCOF<sub>3</sub> (0.5 mmol) was dissolved in acetone (2 mL) under Ar in a flask equipped with a magnetic stirrer and a reflux condenser. Copper phenylacetylide (1.05 mmol), NaI · 2H<sub>2</sub>O (1.05 mmol), and a 0.1 M aqueous solution of PdCl<sub>2</sub> (0.1 mL, 0.01 mmol) were added to the solution. The reaction mixture was stirred at 20 °C for 1 h, then it was ex-

tracted with ether. The ether extract was washed with water and dried over  $\text{Na}_2\text{SO}_4$ . The residue after removal of the solvent was recrystallized from MeOH. *m*-Nitrotolan (0.181 g, 81%) was obtained.

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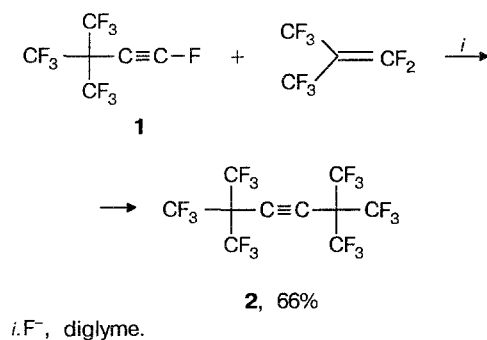
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## Perfluoro-1,2-di-*tert*-butylacetylene

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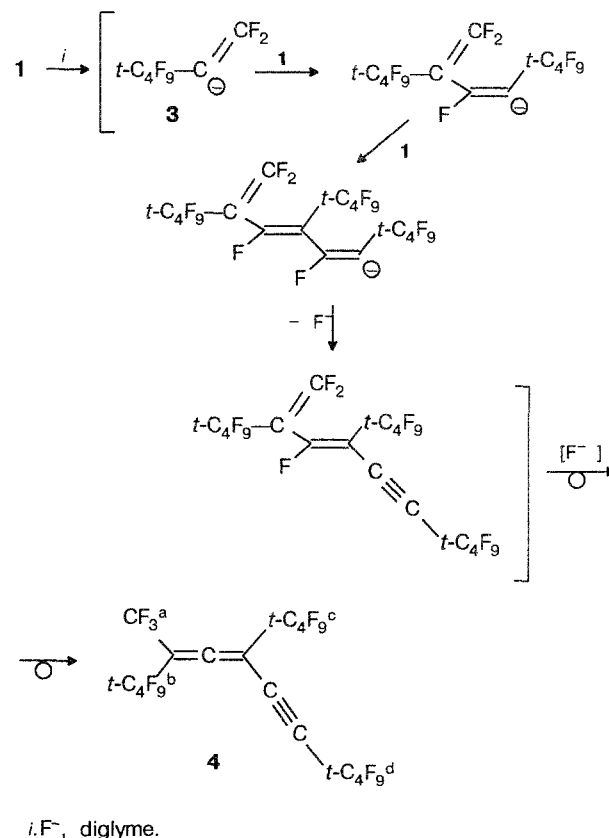
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We found that perfluoro-*tert*-butylacetylene (**1**) reacts with the perfluoro-*tert*-butyl anion generated from perfluoroisobutylene and a catalytic amount of CsF to afford perfluoro-2,2,5,5-tetramethyl-3-hexyne (**2**).



Along with acetylene **2**, the product of the trimerization of the starting acetylene **1** (**4**) was found in the reaction mixture; the formation of the latter is apparently related to the ease of generation and high the reactivity of the concurrently formed vinyl anion (**3**).

Perfluoroisobutylene (6 g) was added gradually to a stirred mixture of freshly calcinated CsF (0.5 g) and anhydrous diglyme (10 mL) at 20 °C; the mixture was stirred for 10 min, then **1** (6 g) in diglyme (5 mL) was



† Deceased.