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SYNTHESIS OF SYMMETRICAL DICARBAZOLE-BIPHENYLS, COMPONENTS OF PHOSPHORESCENT ORGANIC LIGHT-EMITTING DIODES (PHOLEDs) USING ORGANOCUPRATES

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An effective one-stage method is proposed for obtaining symmetrical dicarbazole-biphenyls, components of phosphorescent organic light-emitting diodes through organocuprates of the corresponding N-(bromophenyl)carbazoles. The reaction products were obtained in moderate to high yields.

Keywords: dicarbazole-biphenyl, Gilman cuprate, Lipshutz cuprate, cross coupling, lithiation, energy of the triplet state.

Recently phosphorescent organic light-emitting diodes (PHOLEDs) have attracted significant attention due to the theoretical possibility of achieving high (up to 100%) quantum efficiency through simultaneous electrogeneration of triplet and singlet excitons [1–4]. With the aim of achieving highly efficient electrophosphorescence and reducing such undesirable factors as triplet–triplet annihilation or concentration quenching of luminescence, phosphorescent emitters, which as a rule are complexes of heavy metals, are introduced into basic material [5–7]. 4,4'-Dicarbazole-biphenyls are traditionally used as basic material for PHOLEDs due to the high energy of the triplet state and a high capacity for transporting holes [8–10]. In addition, isomeric dicarbazole-biphenyls such as 3,3'- and particularly 2,2'-dicarbazole-biphenyls, theoretically are more promising materials for PHOLEDs in connection with potentially higher values of triplet state energy, due to the lower conjugation degree of (hetero)aromatic rings. However, the use of traditional synthetic methods successfully applied for the synthesis of 4,4'-dicarbazole-biphenyl namely cross coupling of commercially available diiodo- or dibromobiphenyl according to Ullman or to Buchwald, is significantly limited by the commercial availability

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Dedicated to Academician V. N. Charushin on his 60th birthday.

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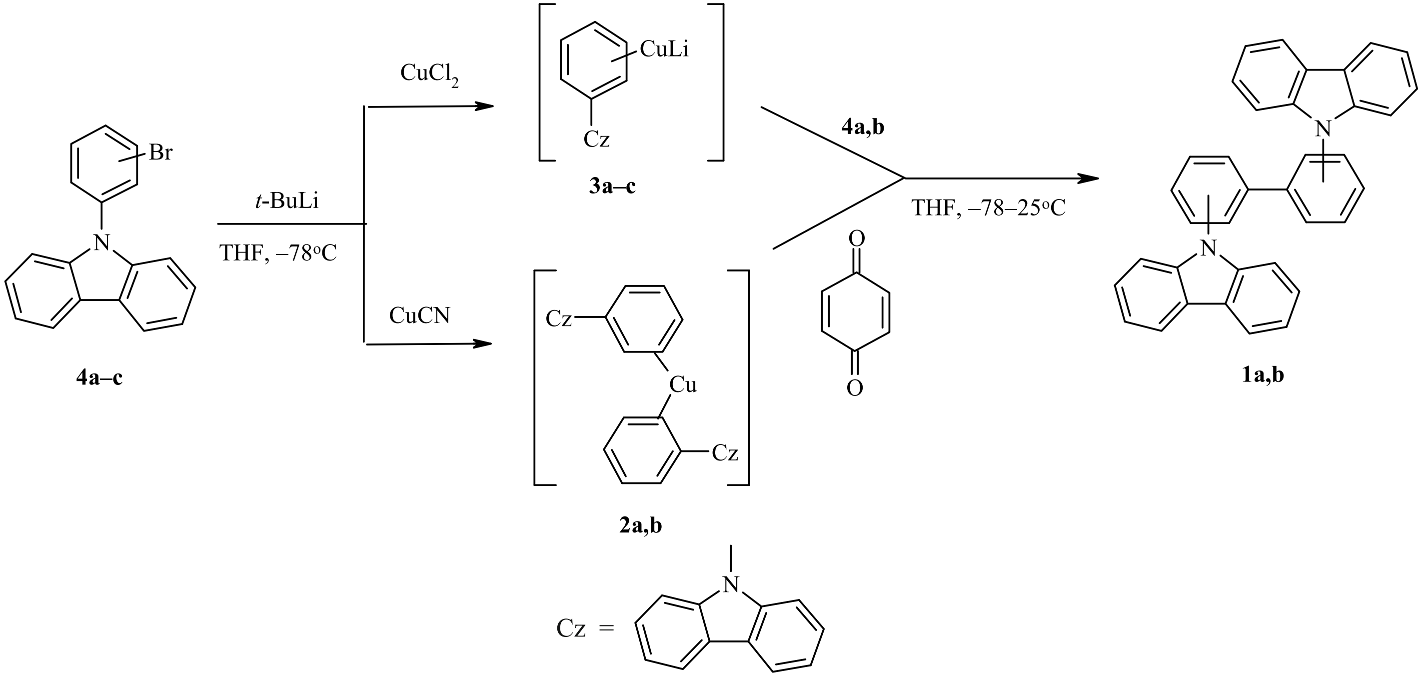
Br
4a–c
t-BuLi
THF, –78°C
CuCl$_2$
CuCN
CuLi
Cz
3a–c
Cz
Cu
Cz
2a,b
Cz =
4a,b
O
O
THF, –78–25°C
N
N
1a,b

of the starting 3,3'- and 2,2'-dihalobiphenyls and also by low yields, as a result of significant steric difficulties [11].

In the present study we have proposed a highly effective one-stage procedure for obtaining symmetrical 2,2'-, 3,3'-dicarbazole-biphenyls **1a,b** and also 4,4'-dicarbazole-biphenyl (**1c**) consisting of the direct cross coupling of corresponding aromatic Gilman [12] cuprates **2a–c** and Lipshutz [13, 14] cuprates **3a–c** in THF solution in an argon atmosphere at –78°C with subsequent warming to room temperature. The cross-coupling products were obtained in 50–76% yield. Cuprates were generated *in situ* by the action of copper(II) chloride or copper(I) cyanide/benzoquinone on solutions of lithium salts obtained by interacting the appropriate N-(bromophenyl)carbazoles **4a–c** with a solution of *t*-BuLi in THF in an argon atmosphere at –78°C.

Characteristic signals for the carbazole fragment were observed in the ^{1}H NMR spectra of compounds **1a–c** as multiplets in the regions of 8.10–8.19, 7.60–7.90, and 7.24–7.34 together with the resonance of protons of the aromatic fragment as a multiplet in the 7.30–7.60 ppm region. A peak for the molecular ion was present in the electron impact (EI) mass spectra of compounds **1a–c**.

Theoretical calculations and preliminary experimental data have demonstrated the high prospects of using dicarbazole-biphenyls **1a–c** as components of PHOLED.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker DRX-400 (at 400 MHz) in $CDCl_3$, internal standard was TMS. The TLC analysis was carried out on Merck silica gel 60 F_{254} plates using UV light. Column chromatography was carried out using Merck silica gel 60. Melting points were measured on a Boetius instrument. Electron-impact mass spectra were recorded on a Varian MAT 311A instrument. All synthetic procedures were carried out in an atmosphere of dry argon.

The starting substances were synthesized by known procedures or are commercially available.

Dicarbazole-biphenyls 1a–c. A. A 1.5 M solution (0.4 ml, 0.6 mmol) of *t*-BuLi in pentane was added dropwise to a solution of compound **4a–c** (0.32 g, 1 mmol) in dry freshly distilled THF (30 ml) at –78°C during 30 min. The obtained solution was maintained for 1 h at –78°C, after which freshly calcined $CuCl_2$ (0.067 g, 0.5 mmol) was added. The mixture was stirred until complete solution of the solid, then stirred at room temperature for 12 h. Water (30 ml) was added, and the mixture extracted with ethyl acetate (3×10 ml). The organic extracts were washed with water (2×10 ml), with 10% aqueous citric acid solution (2×10 ml), with saturated NaCl solution (10 ml), and dried over Na_2SO_4 for 24 h. The solution was filtered, evaporated to dryness in vacuum, and the residue recrystallized from acetonitrile.

B. A 1.5 M solution (0.75 ml, 1.1 mmol) of *t*-BuLi in pentane was added during 30 min to a solution of compound **4a–c** (0.32 g, 1 mmol) in dry freshly distilled THF at –78°C. The obtained solution was maintained for 1 h at –78°C, after which CuCN (0.045 g, 0.5 mmol) was added. The mixture was warmed to room temperature and stirred until complete solution of the solid. After this 1,4-benzoquinone or 2,3,5,6-tetramethyl-1,4-benzoquinone (1.5 mmol) was added at room temperature and the obtained solution stirred for 3 h. The reaction mixture was then worked up as in method A.

2,2'-Dicarbazole-1,1'-biphenyl (1a) [11]. Yield 0.1 g (41%, method A), 0.3 g (62%, method B); mp 242–244°C) (lit. mp 243–244.6°C [11]).

3,3'-Dicarbazole-1,1'-biphenyl (1b). Yield 0.15 g (61%, method A), 0.41 g (85%, method B); mp >250°C (acetonitrile). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.24–7.34 (8H, m, (ArH+$CDCl_3$)); 7.39–7.53 (8H, m, $2C_6H_4$); 7.60–7.90 (8H, m, $2C_6H_4$); 8.19 (4H, d, *J* = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 109.8; 120.0; 120.3; 123.4; 125.7; 126.0; 126.3; 126.7; 130.3; 134.5; 140.9; 142.8. Mass spectrum (70 eV), *m/z* (I_{rel},%): 484 (100) $[M]^+$. Found, %: C 89.01; H 5.05. $C_{36}H_{24}N_2$. Calculated, %: C 89.23; H 4.95.

4,4'-Dicarbazole-1,1'-biphenyl (1c) [15, 16]. Yield 0.22 g (91%, method A), 0.45 g (93%, method B); mp > 250°C (lit. mp 272°C [17]).

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