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Synthesis of nitrile ligands bearing tricarbonyl (η^6-arene)chromium complexes and conjugated spacers

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Abstract

The synthesis of nitrile ligands linked to tricarbonyl (η^6-arene)chromium complexes by conjugated spacers is performed by reacting aromatic bromo nitrile derivatives with tricarbonylchromium-complexed phenylacetylene using Sonogashira coupling reaction. © 2000 Elsevier Science Ltd. All rights reserved.

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Carbon-bridged bimetallic π-conjugated complexes have recently attracted considerable interest due to their physical and chemical properties, leading to potential application such as material with non-linear optical properties. Some examples of the use of heterobimetallic complexes in which the electron-withdrawing and donating properties of two organometallic fragments are combined in order to obtain high first hyperpolarisabilities have been reported.[1] In the search of new combinations of organometallic fragments containing (η^6-arene)chromium complexes, known as typical electron-withdrawing moieties,[2] we were interested in the synthesis of chromium complexes substituted by conjugated chains tailed by a cyano group which could play the role of ligand of an organometallic donor fragment in a further condensation. Indeed, some Fe, Ni and Ru mononuclear complexes with benzonitrile ligand have been described in the literature[3] and showed interesting hyperpolarizability values. In this communication, we describe the synthesis of new nitrile derivatives linked to tricarbonyl (η^6-arene)chromium complexes by different conjugated chains using the palladium–copper-catalysed methodology. This is the first report of coupling reactions between cyano-substituted thiophene (or benzene) derivatives and $Cr(CO)_3$-complexed phenylacetylene.[4]

Complexes **3a**–**d** were obtained by a Sonogashira[5] palladium-catalysed cross-coupling reaction between tricarbonyl (η^6-phenyl) ethynyl chromium complex **1** and various bromo or iodo aromatics substituted by a nitrile moiety **2a**–**d** (Scheme 1). Complex **1** was prepared as recently reported.[4] The halogeno

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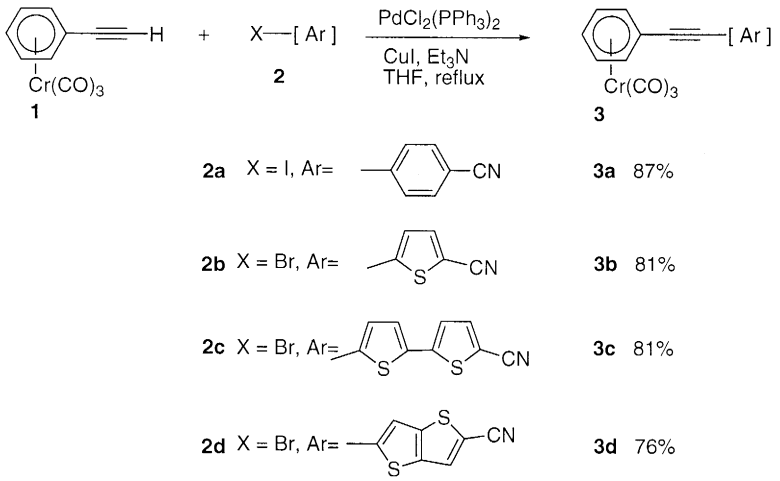
nitrile aromatics **2a**–**d**, are commercially available or prepared using standard literature procedures.[6] As depicted in Scheme 1, the use of classical reaction conditions ($PdCl_2TPP_2$, CuI, Et_3N, THF) readily afforded compound **3a** in 87% yield.



Scheme 1.

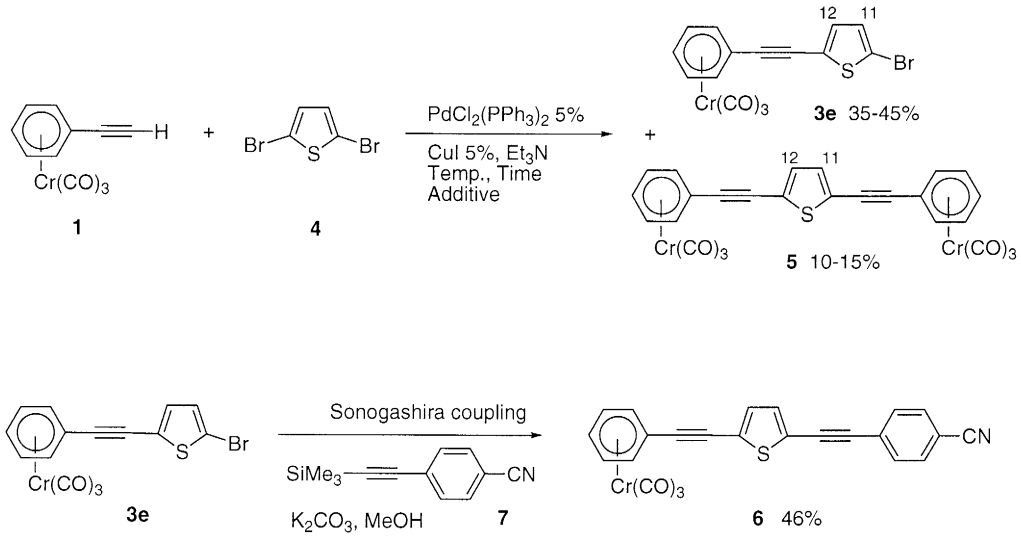
Under similar conditions, complex **1** was coupled with 5-bromo-2-cyanothiophene **2b**, 5-bromo-5′-cyano-2,2′-bithiophene **2c** and 5-bromo-5′-cyanothieno[2,3-*b*]thiophene **2d** to give **3b**, **3c** and **3d**[7] in 81, 81 and 76% yield, respectively.

We next investigated the preparation of compound **6**. As shown in Scheme 2, the synthesis of **6** proceeded through two iterative Sonogashira reactions between compound **1** and 2,5-dibromothiophene **4** and then between compound **3e** and (4-cyano)trimethylsilylethynylbenzene **7**. The first coupling sequence using dichlorodiphenylpalladium(II), copper iodide and triethylamine afforded a mixture of the expected bromothienyl derivative **3e** and the 2,5 di(η^6-phenyl)ethynylthiophene **5** as by-product. The formation of compound **5** can be explained by considering the well-known electron withdrawing ability of the $Cr(CO)_3$ entity which favours the insertion of Pd(0) (in the first step of the catalytic cycle) into the carbon–bromine bond of compound **3e** by comparison to **4**.

Attempts to selectively obtain compound **3e** by varying reaction conditions are reported in Table 1. We found that no reaction took place at 50°C (entry 1) whereas higher reaction temperatures (NEt_3 reflux) were essential for the coupling to give products **3e** and **5**. To overcome the formation of compound **5**, we first used 2 equivalents of dibromothiophene **4**. Surprisingly the **3e**:**5** ratio was found to be dependent on the reaction time. As the chemical shifts and multiplicity of protons H-11 and H-12 were very different, this ratio could be determined by ^{1}H NMR.[8] It is worthy to note that after 30 min, only compound **3e** was detected by ^{1}H NMR spectroscopy (entry 2). This ratio gradually dropped to 3:1 and finally to 2:1 during the course of the reaction (entries 3–5). Moreover, when THF was used as co-solvent (THF:NEt_3 2:1), the observed ratio was only 1.7:1.

On the other hand, the use of a fivefold excess of **4** also afforded a mixture of **3e** and **5** in a 3:1 ratio (entry 7). However, a decrease of the reaction time to only 1 h was observed.

Finally, a 2:1 ratio was also obtained when 1 equiv. of dibromothiophene was used (entry 8), confirming the major role played by the tricarbonylchromium entity in the coupling sequence. Comparing the data obtained entries 4 and 8, we observed that the ratio between complexes **3e** and **5** were almost the same using 1 or 2 equivalents of the dibromo derivative **4**. Compounds **3e** and **5** were isolated in 42 and 12% yield, respectively (entry 5). In the last step, the in situ desilylation of the (4-



Scheme 2.

Table 1

Entry	Eq. of 4	T(°C)	Time(h)	Additive	Ratio 3e / 5 / 1	Yield of 3e(%)
1	2	50	2.5	-	0 : 0 : 1	0
2	2	reflux	0.5	-	1 : 0 : 11	-
3	2	reflux	1	-	3 : 1 : 7.5	-
4	2	reflux	2	-	2 : 1 : 0.2	-
5	2	reflux	2.5	-	2 : 1 : 0	42
6	2	reflux	2.5	THF	1.7 : 1 : 0	33
7	5	reflux	1	-	3 : 1 : 7	-
8	1	reflux	2	-	2 : 1 : 0	27

trimethylsilylethynyl)cyanobenzene **7**[9] and subsequent coupling with **3e** afforded the expected complex **6** in 46% yield.

In conclusion, we prepared new nitrile ligands containing a combination of arene tricarbonylchromium complexes, alkynes and aromatic spacers. Further work is in progress in order to use these new building blocks as ligands in the synthesis of bimetallic complexes with potential activity in non-linear optics. We also pointed out the efficiency of the Sonogashira coupling reaction for the synthesis of substituted acetylenes bearing organometallic moieties. Moreover, resulting from the presence of the tricarbonylchromium entity, the amount of **3e** formed is unexpectedly independent of the ratio of the reactants but dependent on the reaction temperature and time.

Acknowledgements

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7. All new compounds showed satisfactory spectroscopic and analytical data. Typical procedure for product **3d**: The ethynyl complex **1** (137 mg, 0.57 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 0.028 mmol), CuI (6 mg, 0.028 mmol) and compound **2d** (140 mg, 0.57 mmol) were placed under inert atmosphere and dried in vacuo for 30 min. NEt_3 (5 ml) and 10 ml anhydrous THF were then added and the mixture was immediately heated to reflux for 30 min. After cooling to room temperature, the suspension was filtered and the solvents were removed under reduced pressure. The residue was chromatographed on silica gel (diethyl ether:petroleum ether, 3:7) to afford **3d** as an orange solid in 76% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.33 (m, 2H, H_3, H_5), 5.53 (m, 3H, H_2, H_4, H_6), 7.43 (s, 1H, H_{10}), 7.72 (s, 1H, H_{13}); ^{13}C NMR ($CDCl_3$) δ 82.0 (C_1), 87.4 (C_4), 90.1 (C_8), 90.9 (C_6, C_2), 91.1 (C_4), 94.7 (C_3,C_5), 96.4 (C_9), 112.1 (C_{14}), 114.1 (CN), 124.7 (C_{10}), 129.4 (C_{13}), 139.1 (C_{12}), 142.1 (C_{11}), 231.6 (CO); UV–vis (CH_2Cl_2) nm (ε): λ_{max}=330 (14400); IR (CH_2Cl_2) cm^{-1}: 2221 (CN), 1908 and 1976 (CO).
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