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A solution-phase route to a tetraethynylated (cyclobutadiene)cyclopentadienylcobalt complex with a *para*-(1,3,2,4)-substitution pattern†

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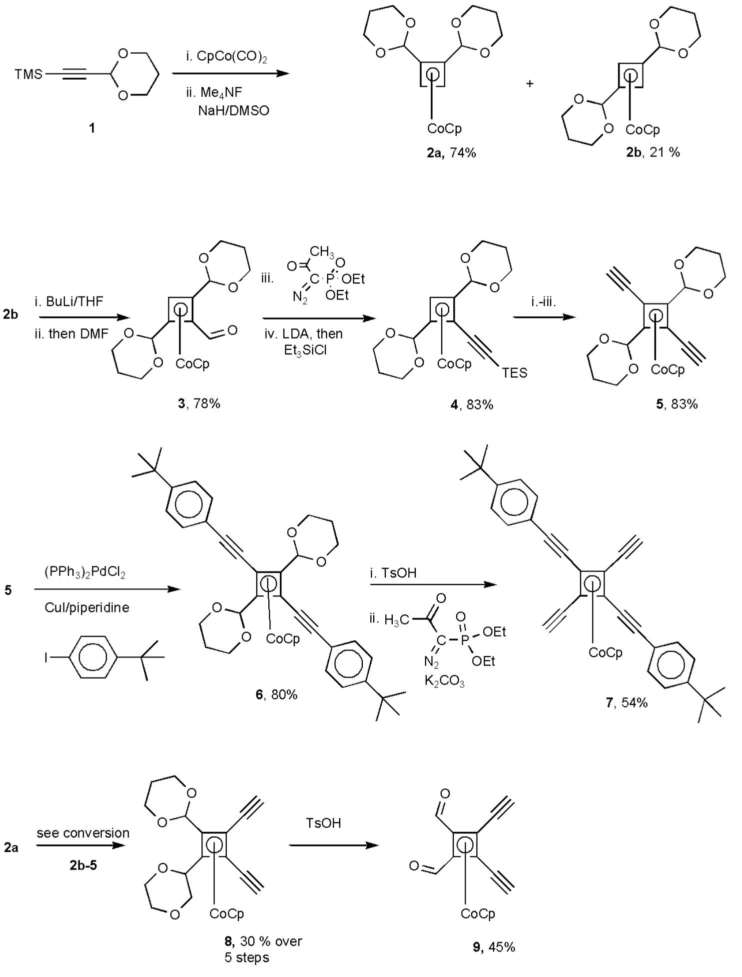
The synthesis of a tetraethynylated, CpCo-stabilized cyclobutadiene complex *via* a metalation/carbonylation/alkynylation route is reported; this synthetic sequence allows, for the first time, the solution phase synthesis of a tetraethynylcyclobutadiene(cyclopentadienyl)cobalt derivative, and sorts the four alkyne substituents into two *para*-related groups.

We have a long-standing commitment in carbon rich organometallics,[1] concentrating our efforts on synthesis, reactions, and properties of multiply alkynylated cyclobutadiene complexes as building blocks for nano-scale carbon-rich[2] objects. Tetraethynylcyclobutadiene(cyclopentadienyl)cobalt complexes[3–7] are valuable due to their robustness, ease of handling and their potential to form super-polycyclic[3,8] organometallic materials. However, the synthesis of these complexes is tedious, requiring a gas-phase flash vacuum pyrolysis step that bottlenecks the amount of tetraethynyl available.[3] These species invariably display a *ortho,ortho*-substituent pattern of their four substituents, a witness to their genesis by a Bergman-type rearrangement. To expand the chemistry of tetraethynylcyclobutadiene(cyclopentadienyl)cobalt complexes, a solution-phase synthesis with control of their regiochemistry would be advantageous.[9]

Reaction of the ethynylated dioxane **1** with $CpCo(CO)_2$ followed by desilylation furnishes a mixture of the two isomeric acetals **2a** and **2b** in a 3.5 : 1 ratio in a combined yield of 95% (Scheme 1).[9] BuLi cleanly metalates **2b** at the cyclobutadiene ring and leaves the Cp-ring intact. We attribute the facile



Scheme 1

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† Electronic supplementary information (ESI) available: experimental, including details of preparation and spectroscopic characterization of all new compounds. See http://www.rsc.org/suppdata/cc/b1/b109848a/

metalation of the four-ring to the enhanced s-character of the C–H-bonds *and* the *ortho*-metalating power of the two acetal groups, that drive this deprotonation reaction selectively.[10]

Workup of the formed anion with DMF provided the complex **3** in 78% yield after chromatography. Ohira's reagent[11] converts the aldehyde group of **3** into an alkyne that is further protected by lithiation and reaction with triethylchlorosilane to give **4**. Repetition of the metalation/carbonylation/alkynylation process with **4** as substrate furnishes the *para*-diyne **5**, in which the protecting group is lost during the K_2CO_3-promoted Ohira reaction. Pd-catalyzed arylation transforms **5** into **6** (80% yield). In the last steps of the reaction sequence, the acetal groups are cleaved off **6**, and a double Ohira reaction converts the intermediate dialdehyde into the title compound **7** in 54% yield.

As a proof of this concept we explored the chemistry of the major isomer **2a** and have transformed it in an analogous reaction sequence into complex **9**, in which two free alkyne groups and two free aldehyde functionalities reside on the cyclobutadiene complex. This material is surprisingly stable and can be manipulated in air at ambient temperature. The dialdehyde **9** is an attractive building block for further elaboration of linear, cyclic and star-shaped organometallic cyclobutadiene architectures.

The tetrayne **7** is stable and can be handled under ambient laboratory conditions without decomposition. Due to the unusual tetragonal symmetry of the ligand we performed a single crystal X-ray structure determination. Suitable needle-shaped specimen were grown from dichloromethane.‡ Fig. 1 shows the ORTEP of **7**; bond lengths and bond angles are in excellent agreement with literature reported values for alkynylated cyclobutadiene complexes.[1,3,4] The four-membered ring is square with angles in the range of 89–91°, and, typical for cyclobutadiene complexes, the alkyne groups are bent away on average by 10° from the side of the cyclopentadienylcobalt fragment. This feature is observed in other tetraalkynylated cyclobutadiene complexes and is attributed to electronic effects.[4]

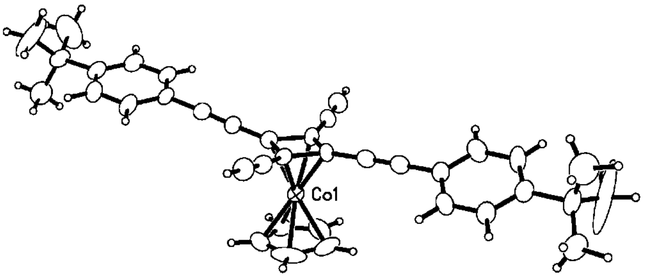

Fig. 1 ORTEP of the tetraethynylated cyclobutadiene complex **7**. Bond lengths and bond angles are in excellent agreement with literature reported values for multiply alkynylated cyclobutadiene complexes.

In conclusion, we have developed a solution-phase route to tetraethynylated, CpCo-stabilized cyclobutadiene complexes. We have executed a stepwise solution-phase synthesis for the hitherto unknown *para*-substituted complex **7**, and could show with the transformation of **2a** into **9** that it will work similarly in the case of the corresponding *ortho*-substituted substrate **2a**. With this methodology, almost complete control over the regiochemistry of the substitution of cyclopentadienylcobalt-stabilized cyclobutadiene complexes is achieved. In future we will report upon the use of these building blocks for novel organometallic oligomers, polymers, cycles and polycycles.

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‡ CCDC reference number 171473. See http://www.rsc.org/suppdata/cc/b1/b109848a/ for crystallographic data in CIF or other electronic format.

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