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Thibaut Jarrosson, Olivier Oms, Gérald Bernardinelli, Alan Williams. Preparation of Star-Shaped Pentapyridyl Ligands for the formation of Giant Fullerene-Like Molecules by coordination Chemistry. CHIMIA, 2007, 61 (4), pp.184-185. 10.2533/chimia.2007.184 . hal-00178192

HAL Id: hal-00178192

<https://hal.science/hal-00178192v1>

Submitted on 7 Jun 2022

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Preparation of Star-Shaped Pentapyridyl Ligands for the Formation of Giant Fullerene-Like Molecules by Coordination Chemistry

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[§]SCS Poster Prize Winner

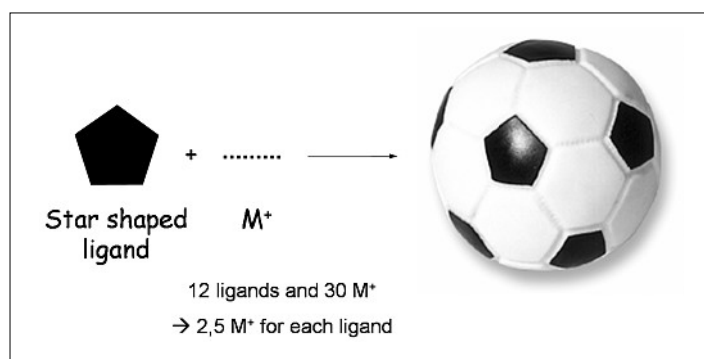
Abstract: We present the syntheses of two new star-shaped penta-ligands containing five pyridyls, which may be considered as starting materials for the preparation of fullerene-like molecules by coordination chemistry. One synthetic strategy is similar to that used for pentaphenylferrocenyl di-*tert*-butylphosphine. The penta-4-pyridyl derivative was prepared in two steps from ferrocene. A second strategy involving a Suzuki cross-coupling reaction with a penta-bromoaryl scorpionate is presented.

Keywords: Coordination chemistry · Ligand synthesis

1. Introduction

One of the major objectives in supramolecular chemistry is the preparation, the design and the synthesis of molecular spheroids.^[1,2] After the first preparation of a molecular container (carcerand) by Cram in 1985, a variety of molecular cages have been prepared through supramolecular self-assembly using multiple hydrogen bonds or metal–ligand coordination.

The basic problem in generating a spherical structure is to induce a curvature of the surface and to avoid the formation of an extended structure in two dimensions. One approach is to use the well-known fact that one cannot assemble pentagons into a planar structure. Thus if one of the hexagons of a regular hexagonal net is transformed into a pentagon, the sheet will buckle. This fact was used in the construction of Buckminster Fuller's geodesic domes, and is the basis of the structure of buckminsterfuller-



Scheme 1.

ene C_{60} which may be regarded as twelve pentagons linked by the vertices (Scheme 1).

Recently, fullerene-like nanoballs were synthesized from pentaphospha-ferrocene and copper derivatives.^[1] The structures are formed by linking cyclo- P_5 rings (pentagonal units) by coordination of copper ions. This provides the formation of five- and six-membered rings in a similar manner to that observed in C_{60} .

2. Synthesis of Pentapyridyl Cyclopentadiene

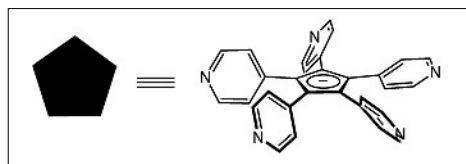
We initially attempted to synthesise free penta(4-pyridyl)cyclopentadiene (Scheme 2) using the procedure of M. Nomura *et al.*^[3] (Fig. 1). The reaction was followed by electrospray mass spectros-

copy and showed the presence of the tetra- and penta-adducts (Fig. 2). The separation of the two products was therefore envisaged, but the penta-adduct proved to be highly unstable towards oxygen forming penta(4-pyridyl)cyclopentadienol. This suggested that the ligand should be stabilized by complexation of a transition metal to reduce the electron density, but several attempts starting from $FeCl_2$ and $CpNa$ (or $CpFe(CO)_2I$ and *t*-BuOK) failed to give the desired pentapyridyl ferrocene. In the last case only the tetrapyridyl ferrocene could be isolated.

3. Synthesis of the Pentapyridyl Ferrocene Derivative 3b

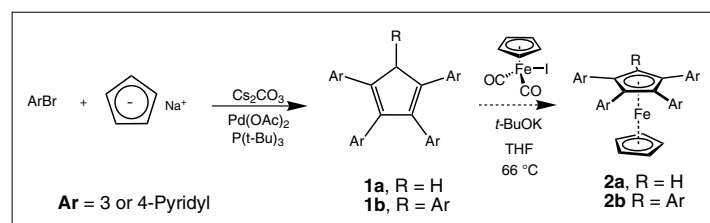
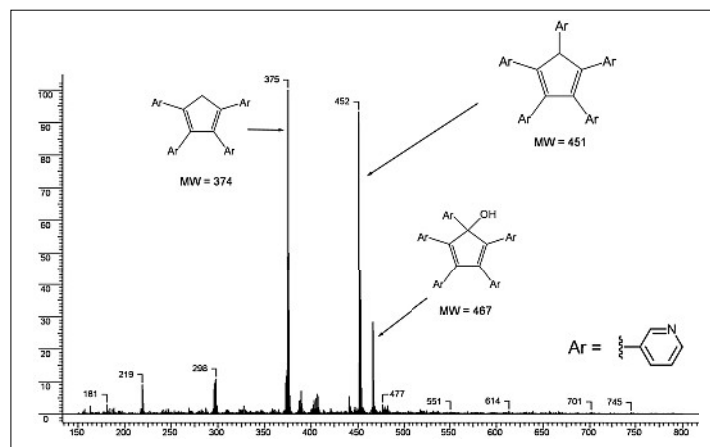
Hartwig *et al.* have reported the efficient incorporation of five phenyl groups

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Scheme 2.

starting from ferrocenyl di-*tert*-butylphosphine (FcP(*t*-Bu)₂)^[4] and we investigated the possibility of introducing the five pyridyl groups using this methodology. The synthesis consists in a palladium-catalysed coupling reaction between FcP(*t*-Bu)₂ and a 4-pyridyl halide in the presence of *t*-BuOK in toluene at reflux. In the first attempts, Pd(OAc)₂ was used as catalyst and 4-pyridyl chloride as reactant (Fig. 3). Tetra-4-pyridylferrocenyl di-*tert*-butylphosphine was the major product, and incorporation of the fifth cyclopentadienyl moiety was not observed. When five equivalents of triphenylphosphine per mol of Pd(OAc)₂ were added to the solution, the (PPh₃)₂Pd(OAc)₂ complex is formed and gave the formation of the penta-4-pyridylferrocenyl di-*tert*-butylphosphine **3a** which was now the major product of the reaction. However, even if 4-pyridyl chloride is used in large excess, a minor quantity of tetra-adduct is still detected. In order to avoid competition between the phosphine group and the pyridine moieties in metal ion coordination, the phosphine oxide derivative **3b** was prepared using 4-methylmorpholine N-oxide as the oxidizing reagent in 75% yield.

Fig. 1. The synthesis of pentapyridyl ferrocene **2b**Fig. 2. Typical ES-MS spectrum of the reaction mixture during the preparation of the pentapyridyl cyclopentadiene **1b**

4. Synthesis of the Star-shaped Ligand **5**

Another approach consisting of adding the pyridyl moieties to a scorpionate derivative was also considered. In the literature, the preparation of a penta(4-bromophenyl)-cyclopentadiene ruthenium scorpionate **4** was described by G. Rapenne *et al.*^[5] After reproducing the synthesis with slight modification (Fig. 4), the coupling reaction of the pyridyl boronic acid ester under Suzuki conditions produced the penta-aryl system **5** in good yield after purification on silica gel (CH₂Cl₂/MeOH 90:10).

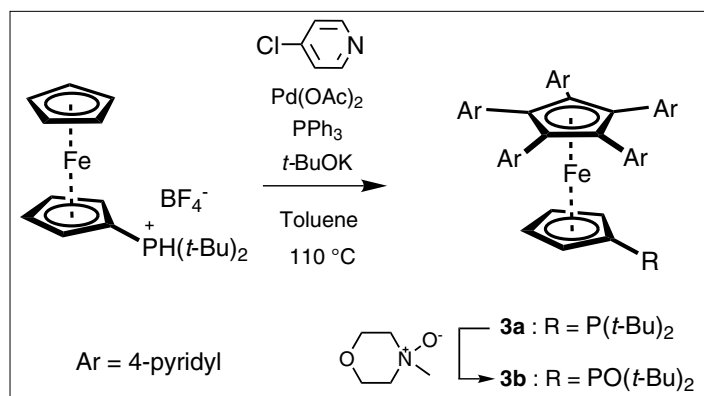
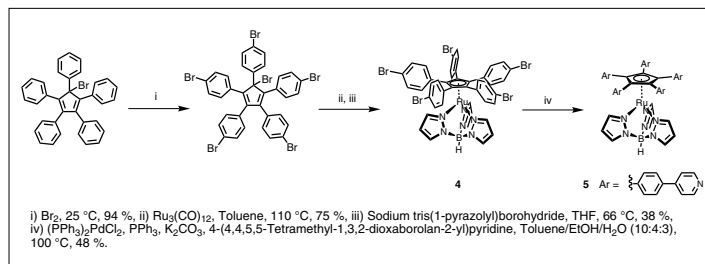
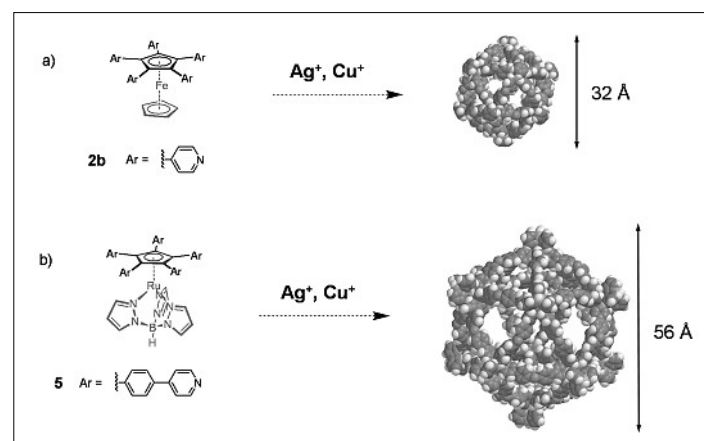
5. Modelling Studies

While coordination studies are currently under investigation and have given promising results for ligand **3b** with Cu⁺, we have

examined the MM3 minimized structures of the predicted systems as shown in Scheme 3. In the presence of Ag⁺ or Cu⁺, ligand **2b** should form a nano-sphere with a diameter of around 32 Å. With the extended penta pyridyl ligand **4**, the diameter of the assembly would be even larger (52 Å).

Received: December 18, 2006

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Fig. 3. Synthesis of the pentapyridyl ferrocene derivative **3b**Fig. 4. Synthesis of the star-shaped ligand **5**

Scheme 3.