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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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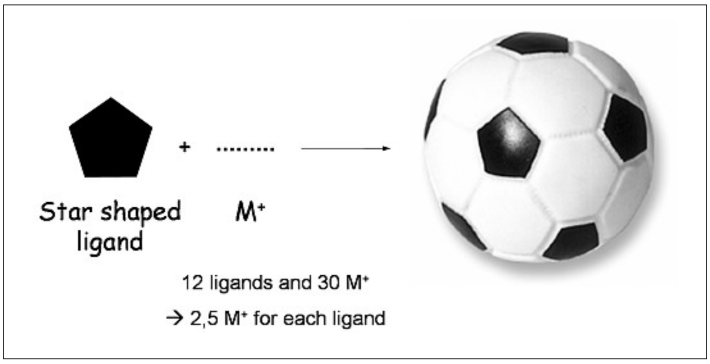
Abstract: We present the syntheses of two new star-shaped penta-ligands containing five pyridyls, which may be considered as starting materials for the preparation of fullerene-like molecules by coordination chemistry. One synthetic strategy is similar to that used for pentaphenylferrocenyl di-*tert*-butylphosphine. 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 spheroidal 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 buckminsterfullerene C_{60} which may be regarded as twelve pentagons linked by the vertices (Scheme 1).



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 spectroscopy 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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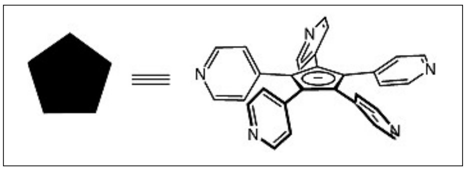

Scheme 2.

starting from ferrocenyl di-*tert*-butylphosphine ($\mathrm{FcP}(t\text{-Bu})_2$)[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 $\mathrm{FcP}(t\text{-Bu})_2$ and a 4-pyridyl halide in the presence of *t*-BuOK in toluene at reflux. In the first attempts, $\mathrm{Pd(OAc)_2}$ 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 $\mathrm{Pd(OAc)_2}$ were added to the solution, the $\mathrm{(PPh_3)_2Pd(OAc)_2}$ 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 monohydrate as the oxidizing reagent in 75% yield.

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 ($\mathrm{CH_2Cl_2}$/MeOH 90:10).

5. Modelling Studies

While coordination studies are currently under investigation and have given promising results for ligand **3b** with $\mathrm{Cu^+}$, we have examined the MM3 minimized structures of the predicted systems as shown in Scheme 3. In the presence of $\mathrm{Ag^+}$ or $\mathrm{Cu^+}$, 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).

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[1] J. Bai, A. V. Virovets, M. Scheer, *Science* **2003**, *300*, 781–783.

[2] M. Scheer, J. Bai, B. P. Johnson, R. Merkle, A. V. Virovets, C. E. Anson, *Eur. J. Inorg. Chem.* **2005**, 4023–4026.

[3] G. Dyker, J. Heiermann, M. Miura, J.-I. Inoh, S. Pivsa-Art, T. Satoh, M. Nomura, *Chem. Eur. J.* **2000**, *6*, 3426–3433.

[4] N. Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, *J. Org. Chem.* **2002**, *67*, 5553–5566.

[5] A. Carella, J. Jaud, G. Rapenne, J.-P. Launay, *Chem. Commun.* **2003**, 2434–2435.

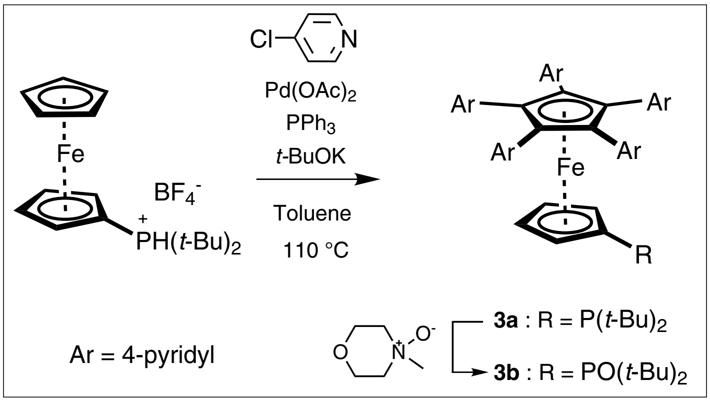


Fig. 3. Synthesis of the pentapyridyl ferrocene derivative **3b**

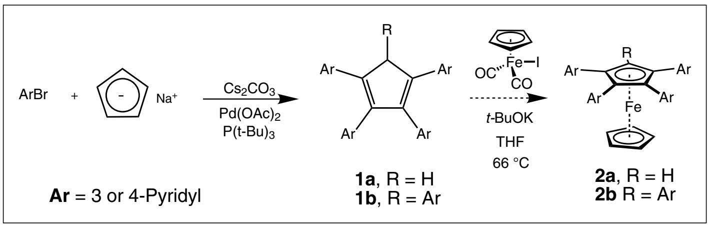
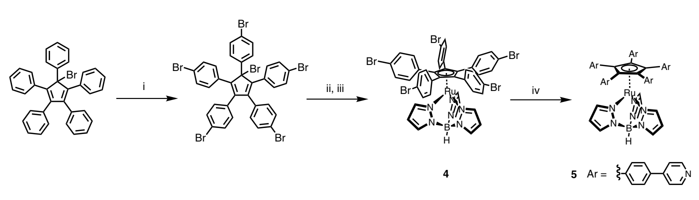


Fig. 1. The synthesis of pentapyridyl ferrocene **2b**



i) $\mathrm{Br_2}$, 25 °C, 94 %, ii) $\mathrm{Ru_3(CO)_{12}}$, Toluene, 110 °C, 75 %, iii) Sodium tris(1-pyrazolyl)borohydride, THF, 66 °C, 38 %, iv) $\mathrm{(PPh_3)_2PdCl_2}$, $\mathrm{PPh_3}$, $\mathrm{K_2CO_3}$, 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine, Toluene/EtOH/$\mathrm{H_2O}$ (10:4:3), 100 °C, 48 %.

Fig. 4. Synthesis of the star-shaped ligand **5**

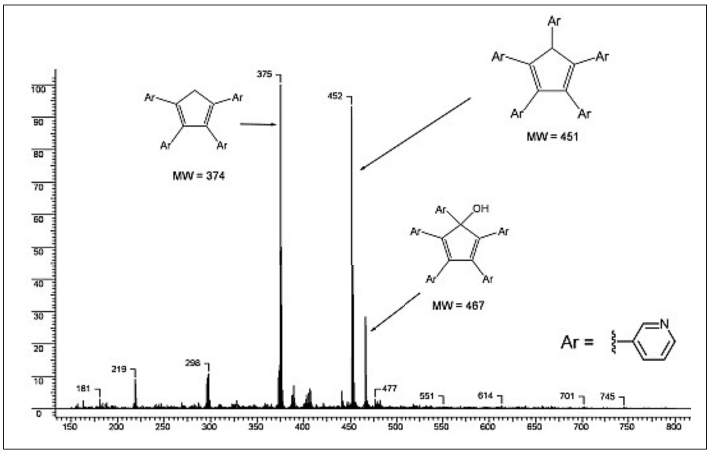
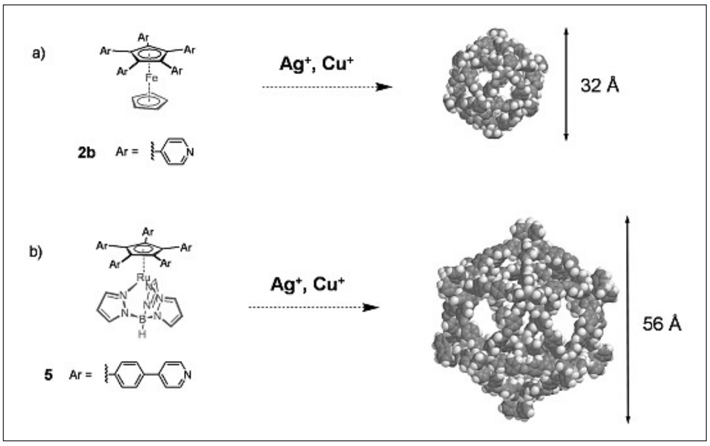


Fig. 2. Typical ES-MS spectrum of the reaction mixture during the preparation of the pentapyridyl cyclopentadiene **1b**



Scheme 3.