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Template synthesis, structure and properties of 4-pyridinylboron-capped iron(II) clathrochelate precursors for Bubnov diallylation reaction☆

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ABSTRACT

Direct template macrobicyclization of three aliphatic, aromatic and dichlorine-containing a-dioxime molecules with 4-pyridinylboronic acid on a Fe^{2+} ion as a matrix afforded the first macrobicyclic tris-dioximates with 4-pyridinyl apical substituents. The macrobicyclic complexes synthesized were characterized using elemental analysis, spectroscopic methods, X-ray crystallography and cyclic voltammetry.

In the early 1990s, Bubnov and co-workers discovered that pyridines, pyrroles and indoles easily undergo reductive *trans*-2,6-diallylation using successive treatment by Scheme 1 with allylic borane (triallyl-, trimethallyl- and tricrotylborane) and alcohol [1–6]. This synthetic procedure gave allylated heterocyclic compounds, which are prospective organic precursors for the preparation of bridged azabicycles and certain alkaloids such as epidihydropinidine, dihydropinidine, and indolizidines [7]. Recently, cage complexes with encapsulated metal ions (clathrochelates [8]) have been tested as transcription inhibitors in the systems of model enzymes (RNA and DNA polymerases, topoisomerase, telomerase, etc.) and were found to be very efficient inhibitors in the case of T7 RNA polymerase [9]; so, they are prospective antiviral and antitumor drug candidates [10]. The presence of reactive terminal groups in apical capping fragments of their macrobicyclic encapsulating ligands allows varying their properties: they help to perform further modification and functionalization of such clathrochelates. In particular, the apically functionalized iron(II) clathrochelates have been described to be the components of both the efficient initiating [11–13] and catalytic [14] systems for olefin polymerization. On the other hand, these clathrochelates (for example, those with 1,4-pentadienyl functionalizing substituents and olefin-containing aromatic and heterocyclic groups [15,16]) themselves are prospective monomers that are useful for obtaining of the new types of metal-containing functionalized linear and cross-linked polymers and co-polymers. Beside, the cage complexes with two apical 4-pyridinyl substituents are structural analogs of 4,4′-bipyridine, which has been widely used as a bridging ditopic N,N′-ligand for the design of various coordination polymers, polynuclear and multicentered transition metal complexes. At the same time, 4-pyridinylboronic acid (4-PyB$(OH)_2$) has been described [17] as a cross-linking (capping) agent for the synthesis of an iron(II) oximehydrazonate clathrochelate with one apical 4-pyridinyl substituent.

In this paper, we describe the synthesis, X-ray structures, spectral and electrochemical properties of the first 4-pyridinylboron-capped clathrochelate iron(II) tris-dioximates. These 4-pyridinyl-terminated clathrochelates were obtained in moderate yields by template condensation of aliphatic and aromatic α-dioximes as well as dichloroglyoxime with 4-pyridinylboronic acid on an iron(II) ion as a matrix (Scheme 2). The aliphatic macrobicyclic iron(II) tris-dimethylglyoximate and tris-nioximate were obtained using standard synthetic procedure [18] in methanol as a solvent. In the case of aromatic α-benzyldioxime, the reaction in a methanol media gave the Tschugaeff-type iron(II) bis-dioximate with 4-pyridinylboronic acid as an axial N-donor ligand. This is the reason why the corresponding 4-pyridinylboron-capped iron(II) tris-α-benzyldioximate was synthesized under severe reaction conditions using a boiling nitromethane as a solvent. The use of trifluoroacetic acid as a solvent in the case of weekly coordinating dichloroglyoxime also allowed avoiding the formation of the corresponding iron(II) bis-dioximate with two 4-pyridinyl-containing axial ligands: this side process is hindered by protonation of their N-donor

☆ Dedicated to the memory of Prof. Mikhail Yu. Antipin, our old friend and co-author, who sadly passed away on February 19, 2013.

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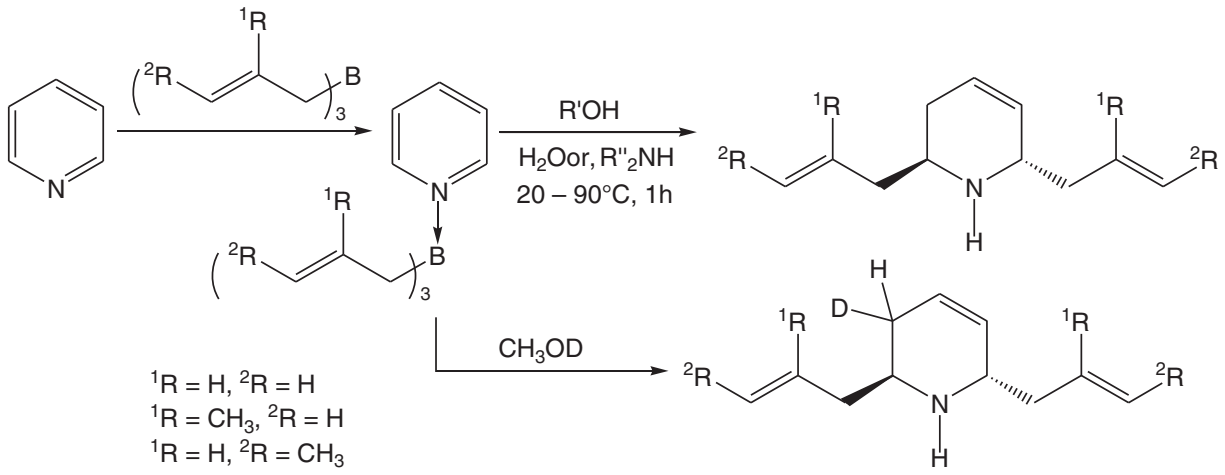
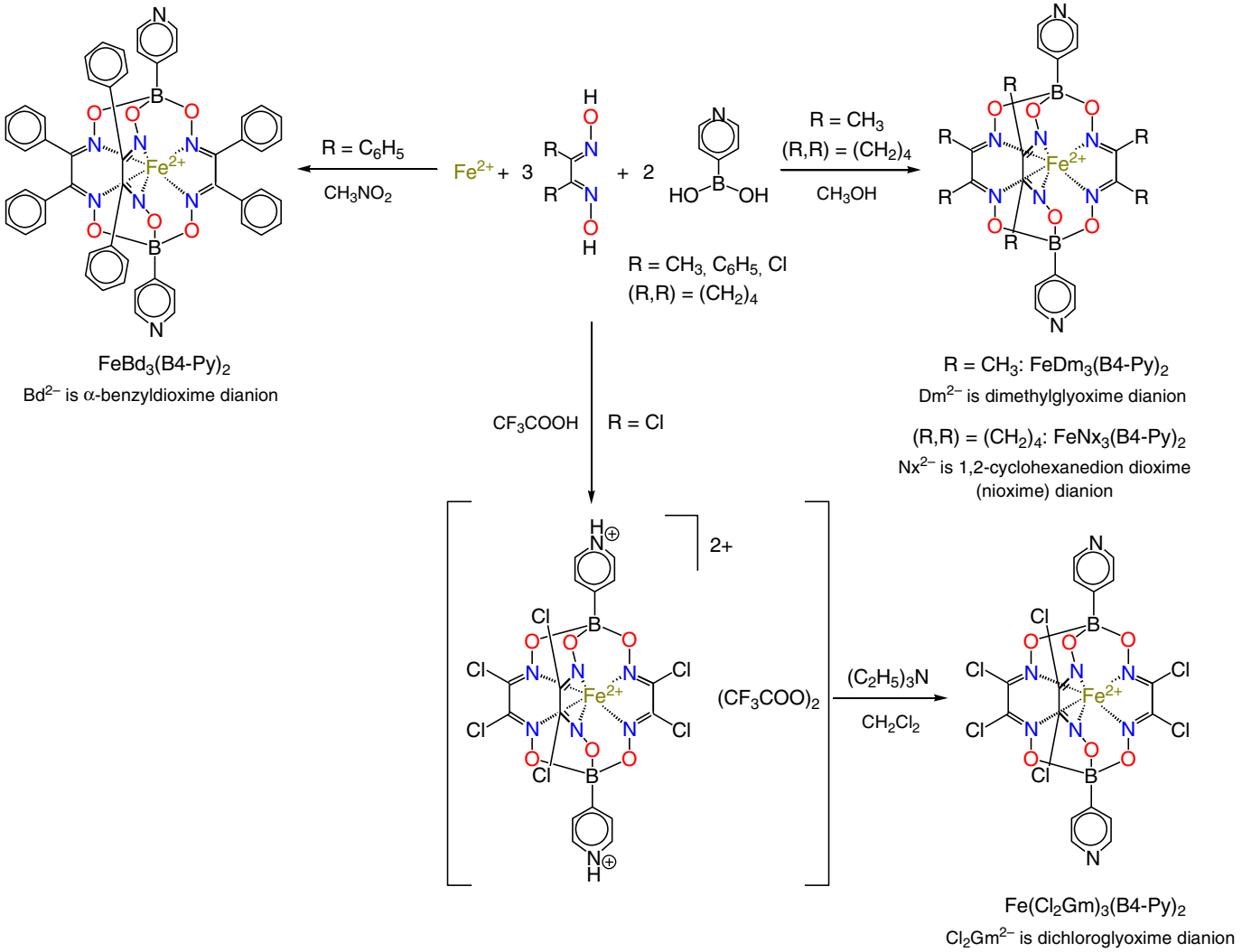


Scheme 1. Reductive *trans*-2,6-diallylation of pyridine.

heterocyclic fragments. As a result, on first stage of the synthetic procedure we obtained a bis-trifluoroacetate salt of the diprotonated clathrochelate dication $[Fe(Cl_2Gm)_3(B4\text{-}PyH)_2]^{2+}$, which then was transformed to the corresponding intracomplex $Fe(Cl_2Gm)_3(B4\text{-}Py)_2$ with triethylamine as a strong organic base.

The complexes synthesized were characterized using elemental analysis, MALDI-TOF mass spectrometry, IR, UV–vis, ^1H and $^{13}C\{^1H\}$ NMR spectroscopies, and by X-ray crystallography (in the case of the iron(II) hexachloroclathrochelate and macrobicyclic tris-dimethylglyoximate).



Scheme 2. Synthesis of the 4-pyridinylboron-capped iron(II) clathrochelates.