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New cadmium-promoted reaction of a C-nucleophile: Synthesis and X-ray structure of the first dicyanopyrazine iron(II) clathrochelate

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ABSTRACT

The first macrobicyclic complex with pendant ribbed dicyanopyrazine substituent was obtained by the new carbanion condensation of the clathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ (where Bd^{2-} and Cl_2Gm^{2-} are α-benzyldioximate and dichloroglyoxime dianions, respectively) with 2,3-dicyano-5,6-dimethylpyrazine in the presence of the cadmium(II) amide as a promoter at r.t. Only one pair of the carbanionic and electrophilic reactive centers is involved in a condensation giving the monosubstituted clathrochelate, whereas the product of the double condensation of its *vic*-dihalogen-containing chelate fragment with *ortho*-dimethylsubstituted pyrazine molecule was not detected. This result is explained by the formation on the first stage of the intermediate dicyanopyrazine carbanion, which is stabilized by the coordination of its heterocyclic nitrogen atom to the cadmium(II) ion. The clathrochelate obtained has been characterized using elemental analysis, MALDI-TOF mass spectrometry, IR, UV–vis, ^1H and $^{13}C\{^1H\}$ NMR spectroscopies, and X-ray diffraction crystallography. The clathrochelate synthesized demonstrates strong CH-acidity: in the presence of strong organic bases its color changes from yellow-brown to violet due to the formation of a clathrochelate anion with highly conjugated azapolyene π-system. Cadmium-promoted condensation is proposed as useful tool to perform other carbanionic reactions as well as to synthesize the functionalized electron-withdrawing heterocycles by alkylation and heteroarylation of their available reactive derivatives.

The *vic*-dinitrile iron(II) clathrochelate with inherent cyano groups and its heteroannulated analog, which are precursors of the polytopic and multicentered hybrid phthalocyaninoclathrochelates, have earlier been synthesized using the reaction of the dihalogenoclathrochelates with copper(I) cyanide – triphenylphosphine complex and the nucleophilic substitution with dimercaptomaleodinitrile, respectively [1,2]. The possible synthetic pathway to the hybrid complexes with methine bridges between the phthalocyanine macroring and the clathrochelate framework is the condensation of these dihalogen-containing precursors with dicyanopyrazine carbanions. However, the use of strong bases in this synthetic procedure to generate the reactive carbanions is limited by side self-condensation of these species as well as by easy destruction of the halogen-containing macrobicyclic trisdioximates in the basic conditions. Earlier, we proposed and successfully used cadmium derivatives of the *O*- and *N*-nucleophiles formed *in situ* with various cadmium(II) amides [3]. These derivatives are soft bases and do not promote the self-condensation, being at the same time reactive in nucleophilic substitutions with halogenoclathrochelate precursors because of a high halophility of the cadmium (II) ions. In the present paper, we describe the use of the cadmium(II) amide $Cd[N(Si(CH_3)_3)_2]$ for the activation of 2,3-dicyano-5,6-dimethylpyrazine (Pyz) as a C-nucleophile.

The nucleophilic substitution of the clathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ [4] proceeds at 0–25 °C with the formation of the monosubstituted macrobicyclic complex only [5]; the product of cycloannulation of dicyanodimethylpyrazine to the formally bifunctional clathrochelate precursor (*i.e.*, the double condensation of its *vic*-dihalogen-containing chelate fragment with *ortho*-dimethylpyrazine molecule) was not detected. This result may be explained by the formation on the first stage of the intermediate dicyanopyrazine carbanion (Scheme 1), which is stabilized by coordination of its heterocyclic nitrogen atom to the cadmium(II) ion with a formation of the chelate organocadmium complex. The deprotonation of the second methyl group does not occur (presumably, due to the electronic effects of the first functionalizing substituent). The complex obtained has been characterized using elemental analysis, MALDI-TOF mass spectrometry, IR, UV–vis, ^1H and ^{13}C NMR spectoscopies, and X-ray diffraction crystallography [6].

The integral intensity ratio of the signals of protons of the phenyl groups of the chelate α-benzyldioximate fragments and those of the aliphatic groups of the ribbed pyrazine substituent in the ^1H NMR

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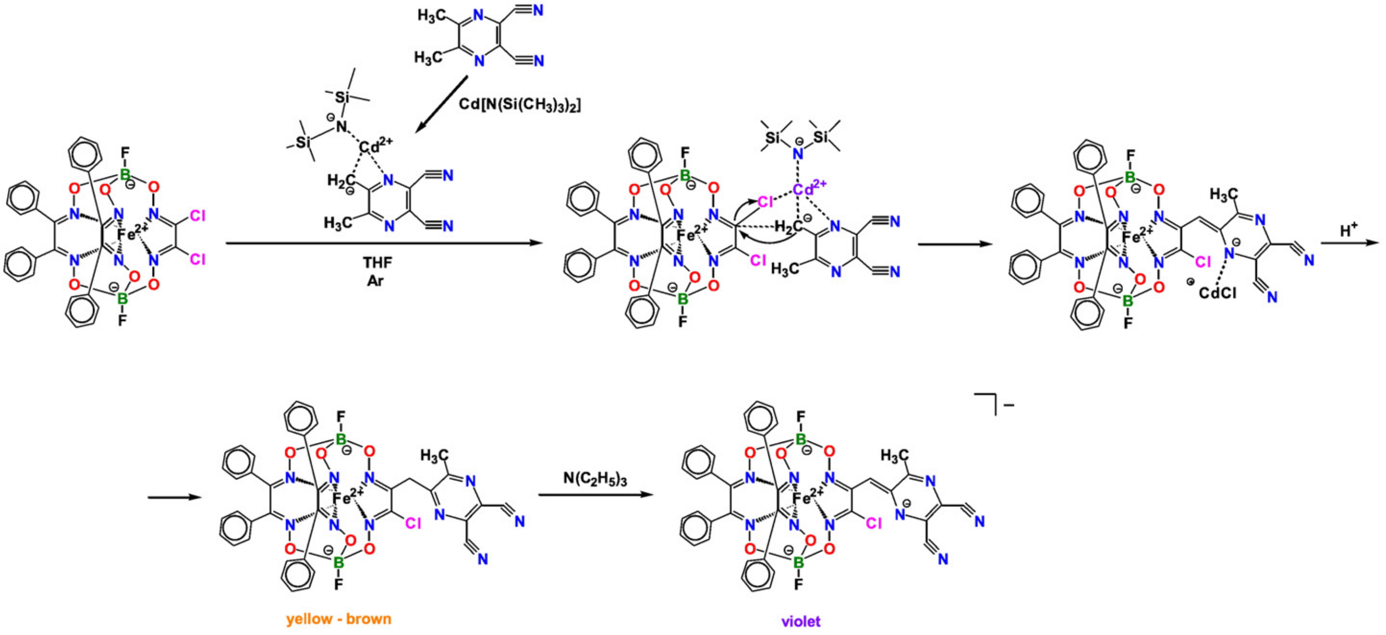

Scheme 1. Cadmium-promoted C–nucleophilic substitution of the iron(II) dichloroclathrochelate with 2,3-dicyano-5,6-dimethylpyrazine.

spectrum confirmed the composition of the complex synthesized, whereas the number of lines in its $^{13}C\{^1H\}$ NMR spectrum indicated the non-equivalence of the azomethine carbon atoms due to the substitution of only one of the two chlorine atoms of the clathrochelate precursor.

Molecular structure of the macrobicycle $FeBd_2(Cl(Pyz)Gm)(BF)_2$ is shown in Fig. 1, the main geometrical characteristics of its clathrochelate framework as well as those for the complexes $FeBd_2(ClXGm)(BF)_2$ {where X are CH_3, NH_2, $N(CH_3)_2$, $N(C_2H_5)_2$, and TempoNH ($TEMPONH_2$ is 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxyl) substituents} are summarized in Table 1. As it can be seen from this Table, the average Fe–N distance (1.906 Å) and the narrow range these distances in the *FeN_6*-coordination polyhedron of the clathrochelate $FeBd_2(Cl(Pyz)Gm)(BF)_2$ fall within are characteristic of the macrobicyclic iron(II) tris-dioximates. An encapsulated iron(II) ion in this molecule is slightly shifted in the direction of its functionalized chelate fragment and the Fe–N distances for this fragment are smaller for this polyhedron, whereas in the molecules of other monoribbed-functionalized clathrochelate iron(II) α-benzyldioximates the corresponding Fe–N distances are greater for their polyhedra. The rigidity of the chelate fragments N=C–C=N causes the bite angles α (half of the chelate N–Fe–N angle) and the heights h of these polyhedra to persist. As a result, the geometry of the clathrochelate molecule $FeBd_2(Cl(Pyz)Gm)(BF)_2$ (the distortion angle φ of its coordination polyhedron is equal to 25.8°) is intermediate between a trigonal prism (TP, $\varphi = 0°$) and a trigonal antiprism (TAP, $\varphi = 60°$).

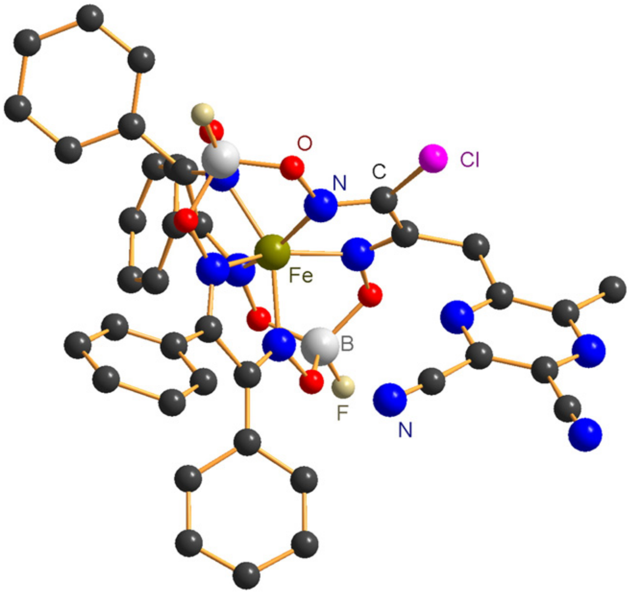

Fig. 1. Molecular structure of the clathrochelate $FeBd_2(Cl(Pyz)Gm)(BF)_2$. Hydrogen atoms are omitted for clarity.

The geometries of the α-benzyldioximate and functionalized chelate fragments are also characteristic of the clathrochelate iron(II) tris-dioximates. The average deviation of atoms of the pyrazine fragment from its *N_4C_6*-mean plain is equal to 0.08(3) Å, and the torsion angle C1–C2–C7–C8 is 65.1(5)°. This fragment forms an intramolecular contact F…π with F2 atom of a neighboring molecule {r(F2…ring) = 1.47(3) Å}. Besides, the short intermolecular contacts Cl1…N5 with r(Cl…N) = 3.17 (3) Å are observed in the crystal studied; so, its clathrochelate entities form the dimers through two contacts Cl…N (Fig. 2).

The clathrochelate obtained demonstrates strong CH-acidity: an addition of the aliphatic amines to its acetonitrile solution causes the change of color from yellow-brown to violet due to the formation of a clathrochelate anion with highly conjugated azapolyene π-system. As a result, three new bands at 531, 581 and 632 nm (Fig. 3) appear, whereas other two bands in the visible region assigned to the Fe*d* → Lπ* charge transfers as well as the intraligand π,π*-transition bands in the UV region are shifted.

Thus, the reaction discovered seems to be a very useful tool to perform other carbanionic substitutions as well as to synthesize the functionalized electron-withdrawing heterocycles by cadmium-promoted alkylation and heteroarylation of their available reactive derivatives.

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