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New Pyrazolino- and Pyrrolidino[60]fullerenes with Transition-Metal Chelating Pyridine Substitutents: Synthesis and Complexation to Ru(II)

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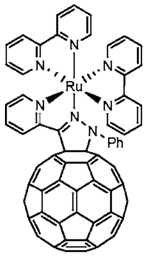
ABSTRACT



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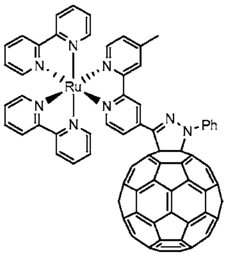

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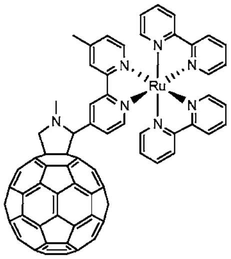

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Three pyridine-substituted fullerene adducts, bis(2,2′-bipyridine)(2′-phenyl-5′-(2-pyridinyl)-2′*H*-[5,6]fullereno(C_{60}-I_h)[1,9]pyrazole)ruthenium-bis(hexafluorophosphate) (1), bis(2,2′-bipyridine)(2′-phenyl-5′-(4-(4′-methyl-2,2′-bipyridinyl))-2′*H*-[5,6]fullereno(C_{60}-I_h)[1,9]pyrazole)ruthenium-bis(hexafluorophosphate) (2), and bis(2,2′-bipyridine)(1′,5′-dihydro-3′-methyl-2′-(4-(4′-methyl-2,2′-bipyridinyl))-2′*H*-[5,6]fullereno(C_{60}-I_h)[1,9]pyrrole)ruthenium-bis(hexafluorophosphate) (3), have been prepared. The common features for these complexes are the short bridges between the fullerene and the pyridine moieties.

In the past years, numerous studies of photoinduced electron-transfer processes using various combinations of donors and acceptors have been carried out.[1,2] Among the combinations, those consisting of a colored transition-metal complex as electron donor and [60]fullerene (C_{60}) as acceptor[1,3] are particularly interesting because of the properties of the C_{60} unit. Most studies have been of multicomponent systems or of assemblies with the two units far apart. We are interested in colored transition-metal complexes of 2,2′-bipyridine (bpy), such as Ru(bpy)$_n$ (n = 2, 3) covalently attached to C_{60}, to study the behavior of assemblies where the distance between the donor unit and the C_{60} acceptor is short. A highly versatile method for the desired functionalization of C_{60} is the addition of 1,3-dipolar reagents to a [6,6]-double bond to form five-membered heterocyclic adducts. As the dipoles are prepared from aldehydes, a wide range of substituents is possible on the heterocyclic unit and different heterocycles can be obtained depending on the choice of dipolar reagent. The use of azomethine ylides with C_{60} to give pyrrolidino[60]fullerenes is well-established,[4] whereas the use of dipoles

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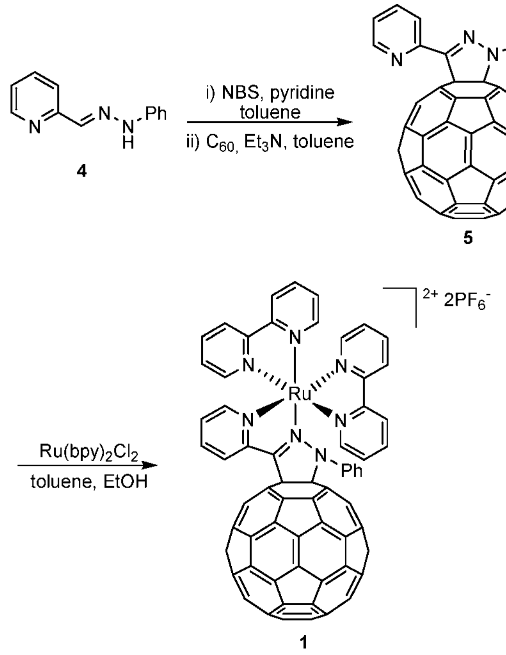
generated from hydrazones to give pyrazolino[60]fullerenes[5,6] has not yet been as widely adopted. As the pyrazoline heterocycle offers a potential coordination site for the donor unit at a very short donor−acceptor distance, this unit is of particular interest.

We are also interested in assemblies only differing in the structure linking the donor to the C_{60} acceptor. Most examples of functionalized C_{60}, including pyrrolidino[60]fullerenes, have a higher reduction potential compared to pristine C_{60}, whereas the pyrazolino[60]fullerenes are reported to have a lower reduction potential.[7] Thus the heterocycle gives access to a modulation instrument of importance for our applications of the assemblies.

In this Letter we present the preparation of three new [60]fullerene-containing pyridine ligands and their corresponding ruthenium−pyridine complexes. In two of the dyads, **1** and **2**, the donor and acceptor are connected via a pyrazoline bridge, whereas the third complex, **3**, contains a pyrrolidine bridge.

The fulleropyrazoline **5**, needed for complex **1**, was prepared by transforming the hydrazone **4** into a nitrilimine using NBS in the presence of pyridine (Scheme 1). Without isolation, the nitrilimine was added to a solution of C_{60} and Et_3N in toluene, yielding pyrazolino[60]fullerene **5** in 48% after purification by flash chromatography.

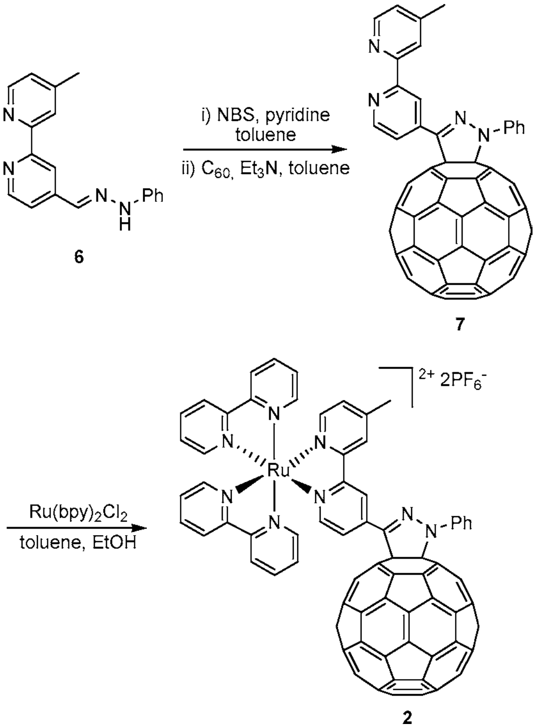
Scheme 1. Synthesis of Fulleropyrazoline **1**



To minimize formation of polyadducts it is important that the C_{60} is completely dissolved before the addition of the dipolar reagent. Toluene is the solvent of choice for dissolving C_{60}, but as also the hydrazone should be completely dissolved for efficient nitrilimine formation, the polarity of the hydrazone is of importance for the outcome of the reaction. Phenylhydrazone **4** was soluble enough in toluene, whereas the more easily prepared 2,4-dinitrophenyl analogue was not. Since polar solvents give better conversion to nitrilimine, we investigated whether it would be possible to use a mixture of solvents where the C_{60} was dissolved in toluene and the nitrilimine formed in dichloromethane. Unfortunately, when adding the dichloromethane solution of nitrilimine to the toluene solution of C_{60}, the fullerene precipitated and no adduct **5** was detected.

Complex **1** was obtained by refluxing **5** with $Ru(bpy)_2Cl_2$ in a mixture of ethanol and toluene (1:1). The mixed solvent was necessary to ensure that all starting materials were sufficiently dissolved. Addition of NH_4PF_6 after the reaction yielded a wine red solid, highly soluble in acetone. The complex is air-sensitive both in solution and in the solid state and was therefore difficult to fully characterize. The UV−vis spectrum of a fresh sample of **1** exhibits features typical for ruthenium bipyridine complexes: broad absorption bands between 400 and 530 nm, which are blue-shifted compared to $Ru(bpy)_2Cl_2$. Within minutes after exposure to air, these features gradually disappear.

Scheme 2. Preparation of Fulleropyrazoline **2**



For the preparation of complex **2**, a similar approach was used (Scheme 2). The precursor for hydrazone **6**, 4′-methyl-2,2′-bipyridine-4-carboxaldehyde (**8**), was obtained from 4,4′-dimethyl-2,2′-bipyridine by oxidation with SeO_2.[8] The fulleropyrazoline **7** was then obtained using the same method as described for **5**, with an isolated yield of 30% after flash

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[6] Espildora, E.; Delgado, J. L.; de la Cruz, P.; de la Hoz, A.; Lopez-Arza, V.; Langa, F. *Tetrahedron* **2002**, *58*, 5821.

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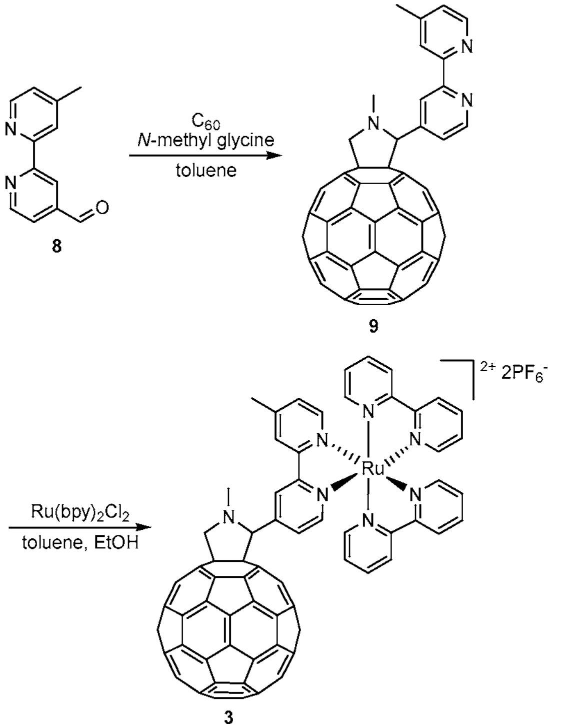
Scheme 3. Preparation of Fulleropyrrolidine **3**



chromatography, but with a minor content of bisadducts with chromatographic properties very similar to those of **7**.

Reaction of **7** with Ru(bpy)$_2$Cl$_2$ following the same procedure as for **1** gave the desired complex **2** which, in contrast to **1**, is quite air-stable.

The fulleropyrrolidine **9** needed for the preparation of the complex **3** was obtained by a one-pot reaction between aldehyde **8**, *N*-methylglycine, and C$_{60}$ (Scheme 3) inspired by the dipolar additions reported by Prato et al.[9] To get an efficient reaction, an excess of aldehyde (5 equiv) is required. We found that approximately 30% of the unreacted aldehyde could be recovered by treatment of the reaction mixture with aqueous Na$_2$S$_2$O$_5$. The thus formed water-soluble bisulfite adduct is washed out of the product-containing organic phase. In addition to making recycling of the aldehyde possible, this prepurification of the reaction mixture is essential in order to obtain a pure product, as separation of excess unreacted **8** from **9** by column chromatography was difficult.

Complex **3** was then prepared as described above and obtained as an air-stable solid.

In conclusion, we have here presented routes to some easily accessible fullerene adducts with metal-chelating properties, demonstrated by their straightforward incorporation into new types of ruthenium−polypyridine complexes.

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Supporting Information Available: Detailed experimental procedures and NMR and UV−vis spectra of products and key intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

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