

## Fullerenes covalently linked to transition metals with organic ligands\*

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**Abstract:** Synthesis of molecules combining both fullerene and metallocene moieties separated by some spacer is discussed in connection with the possible intramolecular charge transfer. Two new kinds of spacers, =CH-CO- and -Pd-P-, have been introduced by using the corresponding reactions. Reaction of diazoacetyl ferrocene and cymantrene with C<sub>60</sub> has been studied in detail and products characterized. 1,1'-Bis(diazoacetyl)ferrocene gave with C<sub>60</sub> 1:1 adduct to which the *ansa*-structure has been assigned on the basis of <sup>1</sup>H and <sup>13</sup>C NMR spectra. Palladium-η<sup>2</sup>-C<sub>60</sub> complex with a bidentate ferrocenyl diphosphine as a ligand has been also prepared.

### INTRODUCTION

Organometallic fullerene chemistry began with the preparation of η<sup>2</sup>-C<sub>60</sub> metal complexes, in which C<sub>60</sub> itself served as a ligand at the transition metal [1]. This line of investigation has been intensely developed as concerned the expansion of the circle of transition metals involved and also in the sense of using higher fullerenes, see [2] for review. The attempt to realize other hapticities, besides η<sup>2</sup>-C<sub>60</sub>, including η<sup>1</sup>(!), met serious obstacles. The stable η<sup>5</sup> complexes were made only with the partial violation of the fully unsaturated fullerene system around the reaction site [3].

On the other hand, when an organometallic fragment is present in an addend, then this group and the fullerene core are *separated* (or, perhaps, *connected*) by a spacer of several atoms, at least, of one atom. Synthesis of the molecules having both fullereryl and metallocenyl fragments is of current interest because of the possible intramolecular interactions between these groups. Fullerenes are known to be strong electron acceptors, whereas organometallic groups may be very different due to the variety of metals and ligands. For example, among the metallocenyl systems there are electron-donating ferrocenes and electron-withdrawing cymantrenes. The degree of electronic communication between the donating and accepting parts of the same molecule should strongly depend on the nature of a spacer. This is the basis for the concepts of molecular wire, molecular switch, unimolecular electronics, etc. [4,5]. As a matter of fact, this is a modern modification of the classical problem of the mutual influence of atoms in a molecule.

### Synthetic approach to the model compounds

The appropriate synthetic routes to these model compounds should be found and their behavior compared depending on the nature of both metallocene and spacer. In this work, we wish to report preparative ways to the compounds under discussion with spacers of two novel kinds, carbon–carbonyl

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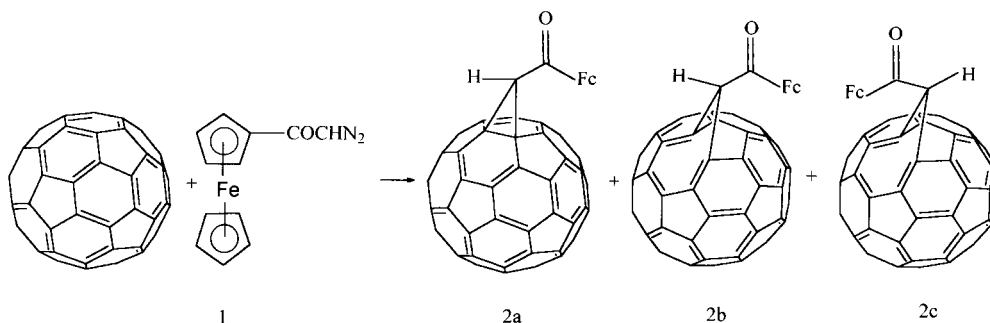
=CH-CO- and palladium-phosphorus -Pd-P-. In order to prepare the first one, we had selected the Wudl reaction with organometallic diazo compounds. To our knowledge, the reaction of mono(chromiumtricarbonyl) complex of diphenyldiazomethane with  $C_{60}$  reported by us as early as 1994 [6], was the first synthesis of a molecule of this class. A special advantage of this approach is the formation of isomeric methanofullerene and fulleroids. The latter gives a possibility to build the continuous chain of conjugation. To compare, in fulleropyrrolidines with a one-carbon spacer [7], a conjugation is not possible in principle. However, the organochromium products appeared to be unstable undergoing easy demetalation.

In the search for more stable model compounds we turned to the diazoacetyl derivatives of ferrocene and cymantrene.

## FULLERENE-METALLOCENE MOLECULES WITH CARBON-CARBONYL SPACERS

### Reaction of $C_{60}$ with diazoacetylmetalloenes

Diazoacetyl derivatives of metallocenes are easy to prepare from the corresponding ketones and they are very good candidates for the organometallic Wudl reaction. We performed reaction of  $C_{60}$  with diazoacetylferrocene (**1**) and diazoacetylcymantrene (**3**) in boiling toluene or *ortho*-dichlorobenzene and observed the remarkable difference in the products. Whereas **1** afforded a mixture of the methanofullerene, **2a**, and two fulleroid isomers, **2b** and **2c** (Scheme 1), as usual for alkyl or aryl diazomethanes, **3** gave a mixture of the methanofullerene, **4a**, and fused dihydrofuran, **4b**, as was reported for organic diazo ketones [8]. This probably reflects the difference in electronic effects of both metallocenes. The Fc-CO group behaves similarly to alkyl or aryl group but the electron-withdrawing properties of the  $Mn(CO)_3$  group enhance the ketone character. Dihydrofuran structure can be formed as a consequence of the mechanism change in the favor of [3+2] carbenoid cycloaddition. Another possibility might be isomerization of the unnoticed fulleroid product in the course of reaction.



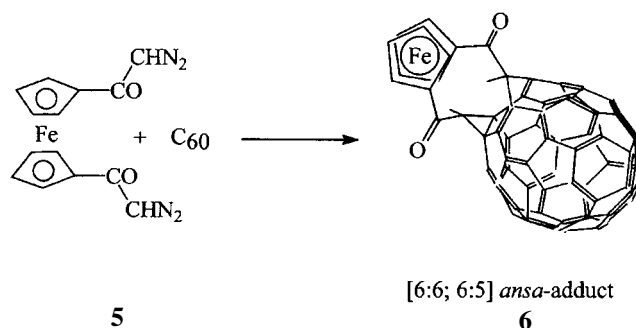
**Scheme 1**

Reaction of **1** was studied in more detail looking at the changes influenced by the additives and reaction conditions. Results are summarized in Table 1, ratios of the products were determined using high-performance liquid chromatography (HPLC), the structures were assigned on the basis of <sup>1</sup>H and <sup>13</sup>C NMR and MALDI-TOF mass-spectra. It turned out that the ratio **2a/2b/2c** in the noncatalyzed reaction of  $C_{60}$  with **1** is mainly determined by the ratio  $C_{60}/1$ , (6,5)-addition being favored by the deficiency of **1**. Tertiary phosphines (PPh<sub>3</sub> or PCy<sub>3</sub>) as additives caused the strong increase of the fulleroid products, **2b** being the major one in the mixture (ca. 75%). Phosphadiazenes RCOCH=N-N=PR<sub>3</sub> are not stable under the reaction conditions, on boiling they dissociate into components. The possible role of PR<sub>3</sub> might be the binding and slow liberation of diazoketone **1** maintaining the large excess of  $C_{60}$ . Rhodium catalysis (by Rh<sub>2</sub>(OAc)<sub>4</sub>) directed the reaction of **1** to the single product of (6,6)-addition, the methanofullerene **2a**.

**Table 1** Effect of additives on the products of the reaction between diazoacetylferrocene and C<sub>60</sub>

Molar ratio C <sub>60</sub> :Fc-CO-CHN <sub>2</sub> :PR <sub>3</sub>			Products (%) in the isomer mixture		
			<b>2a</b>	<b>2b</b>	<b>2c</b>
1	3	0	85	15	0
2	1	0	60	37	3
1	1	1	14	79	7
1	1	0	100	0	0
Rh <sub>2</sub> (OAc) <sub>4</sub> catalyzed reaction			methano- fullerene	fulleroid (H-hexa)	fulleroid (H-penta)

Furthermore, we have synthesized previously unknown 1,1'-bis(diazoacetyl)ferrocene, **5**, and reacted it with C<sub>60</sub>. Three products have been separated, of which the least polar **6** has been characterized. According to MALDI-TOF MS, the ratio of the ferrocene and the fullerene fragments is 1:1. <sup>1</sup>H NMR spectrum evidences that all 8 ferrocenyl protons are different that points to a rigid structure with no element of symmetry. In addition, there are two one-proton singlets mostly downfield (δ 5.85) and mostly upfield (δ 4.19) shifted. In <sup>13</sup>C NMR spectrum, 56 signals of the fullerene core and 10 signals of the ferrocene carbon atoms have been observed. All these data are in accordance with the methanofullerene-fulleroid *ansa*-structure of the adduct **6** with a ferrocene “handle” as shown below (Scheme 2). This means that two additions occurred in different manners, both (6,6) and (6,5), very likely in order to span two remote reaction sites on the surface of the spheroidal molecule.

**Scheme 2**

### FULLERENE-FERROCENE MOLECULE WITH A PALLADIUM-PHOSPHORUS SPACER

Synthetic methods have been recently developed extensively for preparing C<sub>60</sub>M(PR<sub>3</sub>)<sub>2</sub>, M = Pd, Pt. The most useful is the versatile synthesis starting from zerovalent palladium complex Pd<sub>2</sub>(dba)<sub>3</sub>, a ligand, and C<sub>60</sub>, developed by us some years ago and applied then for the synthesis of the first optically active organometallic fullerene complex [9]. Generally, now it is not difficult to synthesize the palladium-fullerene complexes with novel P-ligands at the metal atom. In part, the preparation of ferrocenyl complexes with ferrocenyl phosphines became possible. Recently, we have reported synthesis of the palladium complex **7** with a bidentate ligand 1,1'-bis(diphenyl-phosphino)ferrocene (*dppf*) [10]. It is the first representative molecule with the palladium-phosphorus spacer which has been synthesized in three ways. Cyclic voltammogram of **7** shows two anodic peaks with oxidation potentials +0.87 and +1.22 V

(carbon electrode, *o*-dichlorobenzene, 0.15 M Bu<sub>4</sub>NBF<sub>4</sub> vs. Ag/AgCl/KCl<sub>aq</sub>(sat). as reference electrode). The second potential is nearly equal to that of (*dppf*)PdCl<sub>2</sub>, the first one may involve the palladium atom. The cathodic branch of CVA exhibits three peaks at potentials of -0.69, -1.04, and -1.52 V which may be compared to -0.63, -1.00, and -1.45 V for free C<sub>60</sub>. The three fullerene-centered reductions are shifted toward more negative potential values by about 40–70 mV owing to the transfer of electron density from ferrocene through palladium to fullerene as could be expected. More recently, we have prepared the novel (η<sup>2</sup>-C<sub>60</sub>)PdL<sub>2</sub> complex with *chiral* benzylphenylferrocenyolphosphine as L (in racemic form). In <sup>31</sup>P NMR spectrum two singlets have been observed that correspond to the presence of two isomers, RS (meso) and RR-SS.

## PERSPECTIVES

Further developments in this direction can be expected. Some of them are

- (i) modification of the donor ability of ferrocene by introducing alkyl or other groups;
- (ii) introduction of novel spacers, in the first line, having the chain of conjugation; and
- (iii) application of new metallocenes, ruthenocene being obvious nearest candidate.

One of the close goals could be the synthesis of zwitter-ionic molecules with a negative charge on the fullerene core while a positive charge would be localized in the metallocenyl part.

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