A new heterobimetallic palladium–[60]fullerene complex with bidentate bis-1,1′-[P]₂-ferrocene ligand

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Abstract

A new heterobimetallic palladium–[60]fullerene complex with ferrocene bis-phosphine ligand was prepared using alternative paths: either via addition reaction of $Pd_2(dba)_3 \cdot C_6H_6$ (dba = dibenzylidenacetone) in the presence of 1,1′-bis(diphenylphosphino)ferrocene ($dppf$) to C_{60}, or via electrochemical activation of C_{60} to generate C_{60}^{2-} anions, which then react with $PdCl_2$ and $dppf$ to yield the target complex. The obtained $(\eta^2\text{-}C_{60})Pd(dppf)$ complex was characterized by ^{1}H- and ^{31}P-{^{1}H}-NMR and electronic spectroscopy as well as electrochemically. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

There has been considerable interest in the synthesis, structure, stability, and properties of the Group 10 metal compounds, in which the fullerene cage is attached to organometallic groups to form corresponding π-complexes [1–4]. The first organometallic fullerene derivatives isolated in the individual form were the exohedral complexes of [60]fullerene $\eta^2\text{-}C_{60}ML_2$. These complexes are usually obtained in reactions of [60]fullerene with Pt(0) or Pd(0) compounds stabilized by mono- and bidentate phosphine, olefin, or phosphite ligands. Alternative methods for the preparation of platinum fullerene complexes were developed, which use, as a source of PtL_2 moiety, mercury–platinum bimetallic compounds or bis(aryl)platinum(II) complexes [2c,f]. It is known that fullerenes are able to readily accepted up to six electrons and undergo reversible electrochemical reduction [5]. Recently, we have explored the possibility of synthesizing the exohe-

dral complexes $C_{60}M(PPh_3)_2$ (M = Pd, Pt) from stable ML_2Cl_2 compounds via the electrochemical route. The starting complexes ML_2Cl_2 were reduced by electrochemically generated C_{60}^{2-} dianions to yield corresponding zero-valent complexes ML_2 and neutral fullerene, which further reacted with C_{60} to yield the target $C_{60}M(PPh_3)_2$ complexes [6]. In this paper, we report the preparation of a new [60]fullerene–palladium complex with bidentate ligand, 1,1′-bis(diphenylphosphino)-ferrocene ($dppf$), by using both the ligand exchange reaction and the electrochemical route.

2. Experimental

All the reactions were carried out using the Schlenk technique under an argon atmosphere. The solvents were dried, degassed, and distilled under argon. The ^{1}H-and ^{31}P-{^{1}H}-NMR spectra were recorded with a Bruker AMX-400 FT instrument; the chemical shifts were measured relative to TMS and 1% H_3PO_4, respectively. The ligand, 1,1′-bis(diphenylphosphino)ferrocene, was prepared according to the literature procedure [7].

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## 2.1. Preparation of (η^2-C_{60})Pd($Ph_2PC_5H_4FeC_5H_4PPh_2$) (1)

The solutions of 1,1'-bis(diphenylphosphino)ferrocene (dppf) (111 mg, 0.2 mmol) and [60]fullerene (144 mg, 0.2 mmol) in o-xylene (110 ml) and $Pd_2(dba)_3 \cdot C_6H_6$ (100 mg, 0.1 mmol) in the same solvent (30 ml) were mixed. The obtained green solution was filtered with a pressure filter funnel and left to crystallize at room temperature. After 4 days, the crystals formed were isolated, washed with toluene (10 ml), Et_2O (10 ml), hexane, and dried in vacuo. The mother liquor was concentrated by evaporation under reduced pressure to a volume of 50 ml, and the additional portion of precipitate was isolated. The target complex **1** was obtained as shiny black crystals (206 mg, 75%)

The combustion analysis data were as follows: Found: C, 81.56; H, 2.05; P, 4.09; Fe, 3.58%. Anal. Calc. for $C_{94}H_{28}FeP_2Pd$: C, 81.73; H, 2.04; P, 4.48; Fe, 4.04%. ^{31}P-{^{1}H}-NMR (1,2-dichlorobenzene–C_6D_6, δ ppm): singl., 22.0 (Ph_2-P-Pd). ^{1}H-NMR ($CDCl_3$, δ ppm): 4.23 and 4.70 (m, both AA'BB'X, (C_5H_4)Fe).

2.2. Electrochemical studies

Cyclic voltammetry experiments were performed in o-dichlorobenzene solutions with 0.1 M Bu_4NBF_4 as a supporting electrolyte using a model PI-50-1.1 potentiostat. A platinum working electrode, platinum wire auxiliary electrode and aqueous silver/silver chloride reference electrode were used.

For the electrochemical preparation of complex **1**, C_{60}^{2-} dianions were generated by means of electrolysis of 3×10^{-4} M solution of free C_{60} in o-dichlorobenzene with Pt cathode at a potential of -0.9 V versus the same reference electrode. The obtained deep-purple solution containing C_{60}^{2-} dianions was transferred by argon pressure into a Schlenk vessel with 3×10^{-4} M solution of $PdCl_2$ and dppf in equimolar ratio in o-dichlorobenzene and left overnight. In this manner, fullerene–palladium complex **1** is obtained in near quantitative yield as confirmed by means of UV–vis spectroscopy.
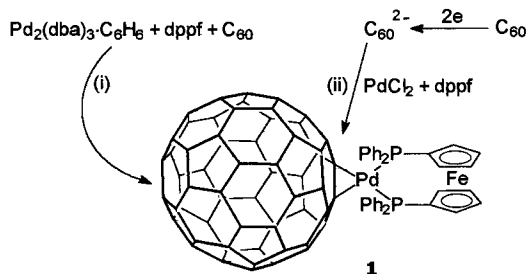
3. Results and discussion

Some years ago, we suggested a new strategy of the one-pot synthesis of η^2-fullerene metal complexes from fullerene, diphosphine ligand, and Pd(0) dibenzylideneacetone complex, $Pd_2(dba)_3$. In particular, this method was used to synthesize first, optically active fullerene metal complexes [2b]. The same approach was used in the present work. Reaction of the solution of the labile $Pd_2(dba)_3 \cdot C_6H_6$ complex in o-xylene with the solution of [60]fullerene and chelating phosphine, dppf, in the same solvent (Scheme 1) yields a green solution of complex **1**, which is only sparingly soluble in o-xylene and in other common organic solvents. Very low solubility allows us to get a refined sample easily, but so far, the crystals obtained have not been suitable for X-ray analysis.

The structure of the crystalline sample of **1** precipitated from o-xylene as a shiny black solid was confirmed by the elemental analysis for C, H, P, and Fe. The analytical data are in good agreement with the molecular formula $C_{60}Pd(dppf)$. The presence of the [60]fullerene fragment in product **1** was also confirmed by the UV–vis spectrum in 1,2-dichlorobenzene, which showed absorption bands at 29 800, 22 400, 15 920, and 14 900 cm^{-1}. The UV–vis spectral data of complex **1** are similar to those of such compounds as (η^2-C_{60})Pd(PPh_3)$_2$; (η^2-C_{60})Pt(PPh_3)$_2$; (η^2-C_{60})Pd[(+)DIOP]; (η^2-C_{60})Pt[(+)DIOP] and other related complexes [2], which comprise one η^2-coordinated metal center attached to the fullerene cage.

Compound **1** is quite stable in the solid state and under an argon atmosphere in aromatic hydrocarbon solutions, but is unstable in CS_2 and $CHCl_3$ solutions. The ^{31}P-{^{1}H}-NMR spectrum of **1** exhibits a single resonance ($\delta = 22.0$ ppm), which is considerably deshielded as compared with that of the free ligand ($\delta = -16.1$ ppm). The two phosphorus nuclei are equivalent. The coordination shift observed for (η^2-C_{60})Pd(dppf) is 38.1 ppm. This tendency is typical for other phosphine complexes as well [1–4].

We have also succeeded in preparation of compound **1** via the electrochemical route. The electrochemical method of obtaining exohedral [60]fullerene metal complexes proposed by us earlier [6] was used. The method is based on the electrochemical production of C_{60}^{2-} anions, which then react with triphenylphosphine Pd(II) and Pt(II) complexes introduced into the reaction mixture. In the case of complex **1**, the compounds used were electrochemically generated C_{60}^{2-} anions, inorganic salt $PdCl_2$ and ligand dppf (see Scheme 1). Deep-purple-colored solution of C_{60}^{2-} anions prepared electrochemically was transferred by argon pressure to a Schlenk vessel which contained $PdCl_2$ and dppf in equimolar ratio. After the transfer the solution turned green, which indicated the formation of the fullerene–palla-

Scheme 1.

dium complex **1**. The latter was confirmed by means of UV–vis spectroscopy.

The electrochemical behavior of complex **1** was studied by cyclic voltammetry. Among similar compounds, literature electrochemical data exist for the fullerene derivatives where C_{60} and ferrocene are covalently bound through pyrrolidine and alkynile bridges [8,9]. For instance, in Ref. [8] it was found that the electrochemical behavior of such compounds is a combination of the redox properties of C_{60} and the ferrocene fragment. As could be expected, the reduction of these complexes involved the orbitals of the fullerene cage, whereas the oxidation occurred on the Fe atom of the ferrocenyl fragment. The effect of the presence of one fragment on the redox properties of the other appeared only as minor differences in the potentials of the redox processes involved: the complex was less readily reduced as compared with free C_{60} because of the electron-donor properties of the ferrocenyl fragment and was less readily oxidized than ferrocene due to the electron-withdrawing effect of the fullerene cage.

However, a particular structural feature of the complex **1** is that the fullerene and ferrocene fragments are bound through the organometallic palladium bridge, which is a redox-active group as well. Therefore, to assign the observed redox transitions to specific redox-active sites of this compound, we have studied its electronic structure by using first the pictorial frontier orbitals approach.

In Ref. [10], steady-state fluorescence and time-resolved flash photolytic investigations of intramolecular electron-transfer processes have been performed for C_{60}(donor)–spacer–Fc(acceptor) dyads and two different quenching mechanisms were suggested: (1) the through-bond electron transfer for the Fc group directly attached to pyrrolydinofullerene or attached through one or two C=C double bonds; and (2) the formation of transient intramolecular complexes for the Fc group attached through long flexible chains containing six or nine σ-bonds.

We were interested in finding the possible types of interaction between the metal atoms in heterobimetallic neutral complex **1**. In this connection, we considered the frontier orbital interactions in a simpler model complex, (*dppf*)Pd(Ph₃P) (**2**). A similar complex of bivalent palladium, [(*dppf*)Pd(II)(Ph₃P)](BF₄)₂ (**2²⁺**), which differs from complex **2** only in the oxidation state of the palladium atom, was earlier characterized by X-ray diffraction studies [11]. It was shown that the ferrocene fragment in that complex is bent, with the distance between the Fe and Pd atoms 2.877 Å, which suggests the overlapping of their orbitals.

In constructing the frontier orbitals of complexes **2** and **2²⁺**, they were considered as combinations of two fragments: the distorted ferrocene molecule (in bent form, symmetry C_{2v}) and the planar fragment PdL₃,

L = Ph₃P, (symmetry C_{2v}). Molecular orbitals of similar fragments were considered in Refs. [12,13]. When combining these fragments into complex **2²⁺**, the LUMO of the 14-electron d^8 PdL₃ fragment interacts with the HOMO of the ferrocene fragment as presented below:

a₁ bonding interaction
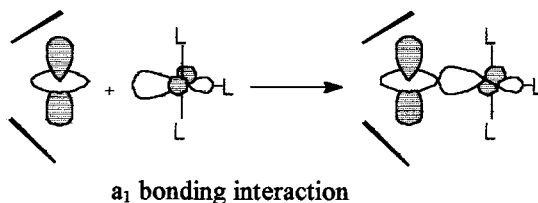
Here the Fe atom of the ferrocene fragment acts as a σ-donor for the Pd atom.

In complex **2**, the a_1 orbital of the 16-electron d^{10} PdL₃ fragment is filled, and therefore the a_1 antibonding combihation of the a_1 d_{z^2} Fe and a_1 $d_{x^2-y^2}$ PdL₃ orbitals will be the HOMO of the complex:

a₁ antibonding interaction
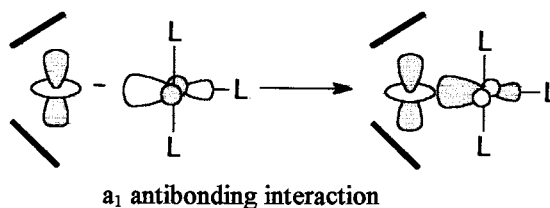
Here the Fe atom of the ferrocene fragment is a weaker σ-donor than Fe in complex **2²⁺**.

On the other hand, two degenerate empty molecular orbitals of the bent ferrocene moiety (d_{xy} or d_{yz} of Fe, which are in an antibonding combination with e_{1g} orbitals of the ensemble of two stacked Cp⁻ ligands), interact with the HOMO of the PdL₃ fragment to give two degenerate orbitals of b_2 and a_2 symmetry, in which the ferrocene fragment acts as a π-acceptor:
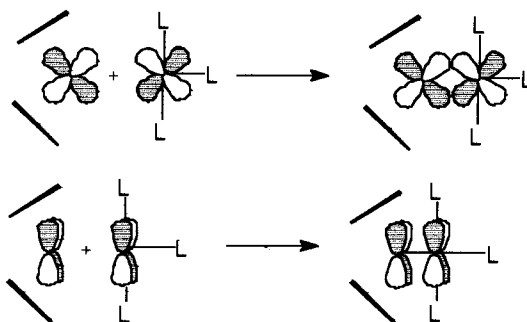
Therefore, Fe atom in bent ferrocene acts as π-acceptor as well as a σ-donor towards PdL₃ fragment.

As a more acceptable model of complex **1**, molecular orbitals of 1,1′-bis(diphosphino)ferrocene (*dpf*) phosphinopalladium complexes, (*dpf*)Pd(PH₃) (**3**) and [(dpf)Pd(PH₃)]²⁺ (**3²⁺**), were calculated using the modified INDO/1 semi-empirical method ZINDO/1 [14]. The structures of the complexes were obtained using the ZINDO/1 method in the HyperChem program (Hypercube Inc., Gainesville, FL, USA). The
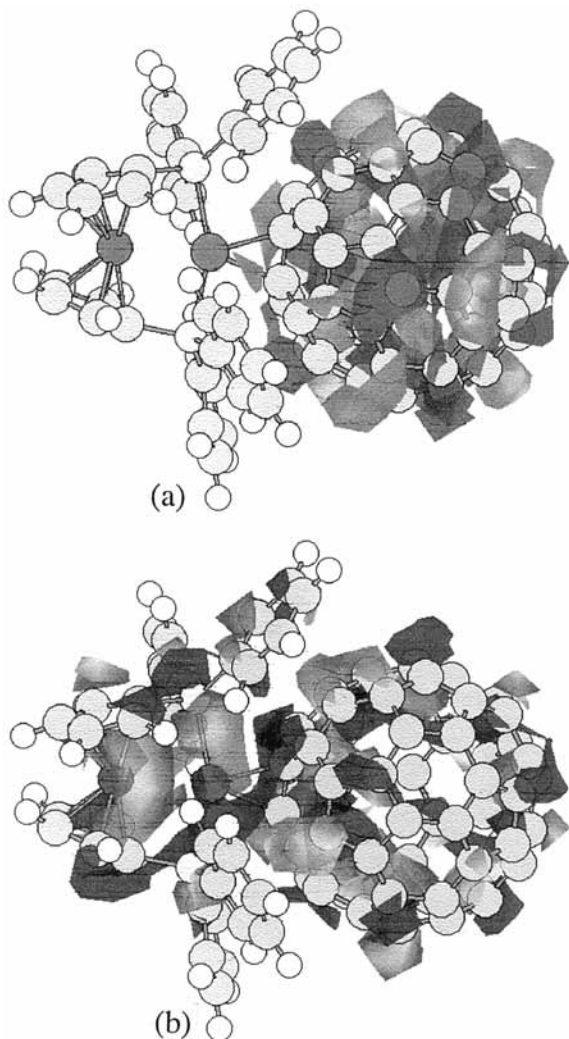
Fig. 1. LUMO (a) and HOMO (b) of $C_{60}Pd(dppf)$ as calculated using the extended Hückel method for a geometry optimized with the MM+ molecular mechanics method.
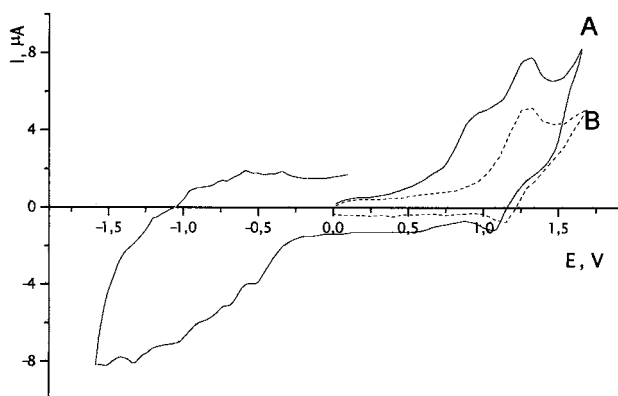

Fig. 2. Cyclic voltammogram of (A) $C_{60}Pd(dppf)$ and (B) $(dppf)PdCl_2$ (carbon electrode, o-dichlorobenzene, 0.15 M Bu_4NBF_4, Ag | AgCl | KCl (sat.)).

convergence condition was that the gradient was lower than 10 cal mol^{-1} $Å^{-1}$. All parameters used in ZINDO/1 were the default parameters in the HYPER-CHEM program. In the both calculated structures the ferrocene fragment has a bent antiprismatic configuration with Fe–Pd distance 2.915 Å in **3** and about 3 Å in 3^{2+}.

Also, we calculated the entitled complex **1**. The geometry optimization of this molecule was carried out using the molecular mechanics MM+ method in the HYPERCHEM program (an all atom force field method). We used the Polak–Ribiere algorithm; the total energy gradient was lower than 1 cal mol^{-1} $Å^{-1}$.

The calculated geometry of molecule **1** can be compared with those obtained in [2a] for $C_{60}Pd(PPh_3)_2$ from X-ray diffraction data (the latter are given below in parentheses): Pd–Fe distance (2.616 Å); bond lengths (in Å): C–C 1.365 (1.447); Pd–C 2.135 (2.08 and 23.133), Pd–P 2.331 and 2.334 (2.330 and 2.315); bond angles (in °): CPdC 37.3 (40.2), CPdP 156.2 (109.7). Such changes in geometry can be understood because molecule **1** is stereochemically more rigid than $C_{60}Pd(PPh_3)_2$.

The single-point molecular orbital calculations were carried out using the extended Hückel method [15]. The calculated frontier orbital pictures of complex **1** (Fig. 1) show that the LUMO is localized on the C_{60} fragment and, therefore, the primary electronic changes during the reduction of this complex are localized on the C_{60} moiety.

The calculated HOMO is spread through the whole molecule. However, from the HOMO picture in Fig. 1, it is difficult to say where the primary electronic changes is localized in the electrochemical oxidation of complex **1**: on Fe, Pd, or C_{60}?

Let us proceed again from model complex **2** to the target complex **1** by substituting the equatorial triphenylphosphine ligand for C_{60}. The latter is a strong acceptor, which results in lowering the frontier orbitals of the palladium fragment. The lowering of the LUMO energy of the PdL_3 fragment gives rise to an increase in the σ-donor ability of the ferrocene fragment, while lowering its HOMO energy results in a decrease in its π-donacity. Therefore, the two effects result in a decrease in the electron density on the Fe atom as compared with complex **2**.

The electrochemical oxidation of complex **1** can in principle involve the orbitals of either Fe or Pd atoms. Cyclic voltammograms of complex **1** (Fig. 2) feature two anodic peaks located at +0.87 and +1.22 V (vs. Ag | AgCl | KCl$_{aq.}$ (sat.) reference electrode). The second peak is electrochemically reversible and probably belongs to the ferrocene moiety. From the above discussion of the interaction between the orbitals of the ferrocene and palladium fragments, it follows that the

most likely localization of the first oxidation process involves the palladium atom:

$$(\eta^2\text{-}C_{60})Pd(dppf) - 2e^- \rightarrow [Pd(II)(dppf)]^{2+} + C_{60}$$
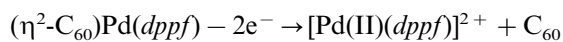
Further oxidation of complex **1** involves the orbitals of the iron atom in $(dppf)Pd(Solvent)_2]^{2+}$. The potential of this process ($+1.22$ V vs. Ag | AgCl | KCl$_{\text{aq.sat.}}$) is almost equal to the oxidation potential of $(dppf)PdCl_2$ and is somewhat more positive than the oxidation potential for free 1,1′-bis(diphenylphosphino)ferrocene ($+0.97$ V vs. the same reference electrode). Such a shift in the *dppf* oxidation potential due to coordination with the Pd-containing group must be related to strong σ-acceptor effect of the latter fragment, as was demonstrated above. The cathodic branch of the CVA obtained for complex **1** demonstrates, along with minor peaks of the reduction of free C_{60}, the peaks at potentials of -0.69, -1.04, and -1.52 V. They can be attributed to the electrochemical reduction of complex **1** involving the orbitals that are mostly localized on C_{60}.

Therefore, our electrochemical studies suggest that the Pd-containing bridge in complex **1** demonstrates electrochemical activity in the anodic potential region only. The fullerene and ferrocenyl fragments of **1** retain their electrochemical properties that they show in the individual form and demonstrate reversible electrochemical behavior in the cathodic and anodic regions, respectively. However, the redox transitions of these fragments occur at slightly different potentials: the oxidation peak of the ferrocenyl group shifts into the anodic direction, whereas the reduction potentials of the fullerene cage become more cathodic. These facts demonstrate that the charge transfer in complex **1** occurs from the Fe atom to the fullerene cage via the Pd bridge.

Acknowledgements

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