

A NEW TYPE OF EXOHEDRAL PALLADIUM-BRIDGED HETEROBIMETALLIC [60]- AND [70]-FULLERENE DERIVATIVES

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New electrochemical route to the interesting type of heterometallic exohedral palladium-bridged fullerene derivatives with diphenylphosphinometalocenyl ligands has been proposed. The method is based on the indirect electron transfer process, in which the fullerene plays the role of a mediator and one of the building blocks of the target complexes, simultaneously (scheme 1). Therefore, the presented method includes the advantages of mediator process - low overvoltage, small impact of side reactions at the electrode surface - and there is no need to add in the solution any additional compounds.

The voltammetric study of obtained heterobimetallic exohedral complexes has been performed. They consist of two fragments, one of that is redox-active in cathodic area (the fullerene cage), and the other is redox active in anodic area (cyclopentadienyl-transition metal moiety), linked through diphenylphosphine palladium bridge, which is also redox-active. Hence, these compounds can be considered as an interesting example of charge transfer systems and maybe promising as a catalysts.

An interesting correlation between electrochemical and X-ray crystallographic data has been revealed (Fig.1). The reduction potentials of η^2 -type organometallic complexes reflect the degree of fullerene C-C double bond elongation due to coordination with the metal atom. The longer C-C bond is, more difficult is the reduction of a complex. That reflects intramolecular electron transfer processes

Acknowledgment

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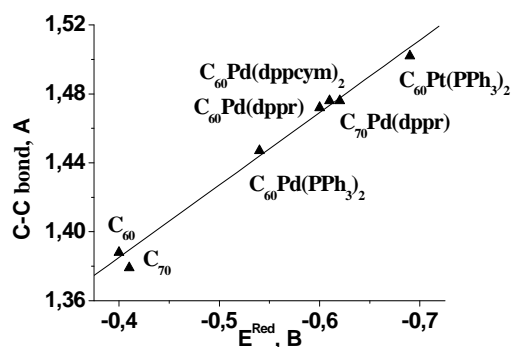
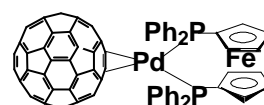
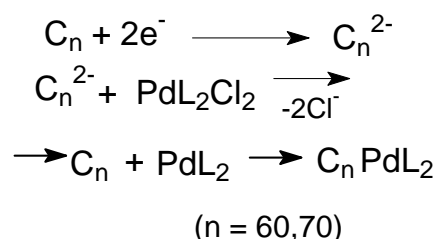
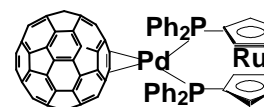


Fig 1. Plot of C₁-C₂ bond lengths vs. reduction potentials of η^2 -fullerene complexes

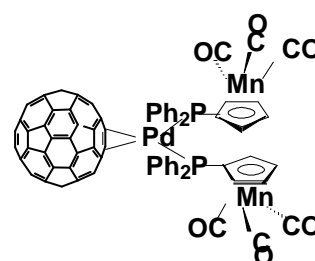
Scheme 1:



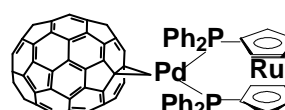
C₆₀Pd(dppf)



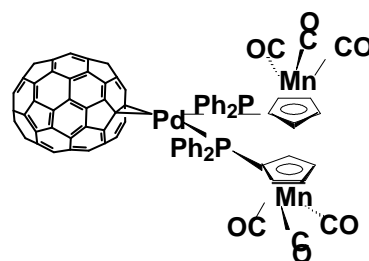
C₆₀Pd(dppr)



C₆₀Pd(dppcym)₂



C₇₀Pd(dppr)



C₇₀Pd(dppcym)₂