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Sandwich complexes of iron and ruthenium with the semiconducting aromatic hydrocarbon picene

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Dedicated to Prof. Armando J.L. Pombeiro in recognition of his diverse contributions
to the organometallic chemistry and on the occasion of his 70th birthday.

Abstract

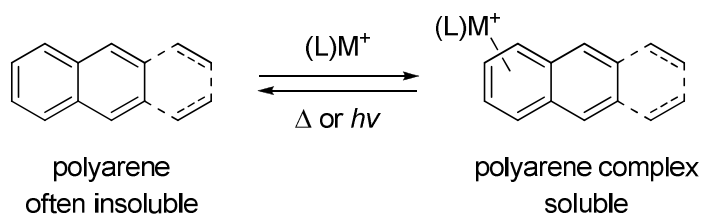
Pentacyclic aromatic hydrocarbon picene $C_{22}H_{14}$ was synthesized by the improved two-step procedure from 1-naphthaldehyde in ca. 50% total yield. Reaction of picene with ferrocene in the presence of $AlCl_3$ produced the binuclear iron complex $[(CpFe)_2(C_{22}H_{14})](PF_6)_2$. Reactions of picene with $[Cp^*Ru(MeCN)_3]PF_6$ produced mono- or binuclear complexes depending on the concentration and ratio of reactants. The structures of the binuclear iron complex and the mononuclear ruthenium complex were established by X-ray diffraction analysis. Irradiation of the iron complex regenerated free picene; this method is proposed for purification and deposition of insoluble aromatic hydrocarbons.

Keywords: picene, iron, ruthenium, arene complexes, sandwich complexes

1. Introduction

Polycyclic aromatic molecules (polyarenes) attract enormous attention owing to their luminescent and semiconducting properties.^{1,2} However, the application of polyarenes is often limited by extremely low solubility, which prevents their purification and deposition of thin films from solutions. The classical solution of this problem is based on attachment of long alkyl substituents to the polyarene molecules. However, such substituents not only improve the solubility of polyarenes but also change their packing in the solid state and therefore have unpredictable and often detrimental effect on their properties. Herein we propose an alternative possible solution for this problem, which is based on reversible formation of soluble metal π -complexes of polyarenes (Scheme 1).

In order to investigate this idea we have chosen one of the classic semiconducting molecules - pentacyclic aromatic hydrocarbon picene $C_{22}H_{14}$ (Scheme 2).^{3,4} We have decided to synthesize picene complexes with $[CpFe]^+$ and $[Cp^*Ru]^+$ fragments, because iron and ruthenium complexes $[(C_5R_5)M(arene)]^+$ are known to have high chemical stability⁵ as well as the ability to release arenes upon irradiation.^{6,7} Iron and ruthenium complexes have been previously obtained for many polyarenes, including pyrene, rubrene and coronene.^{8,9} However, to the best of our knowledge, complexes of picene with any of transition metals have not been reported.



Scheme 1. The proposed approach for conversion of polyarenes into soluble forms.

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