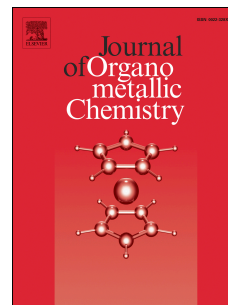# Accepted Manuscript

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

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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 stability[5] 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.
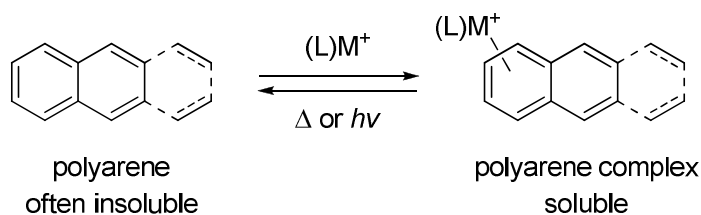

Scheme 1. The proposed approach for conversion of polyarenes into soluble forms.

2. Results and discussion

We synthesized picene by the improved two-step procedure (Scheme 2). The McMurry coupling[10] of 1-naphthaldehyde produced 1,2-di(naphthyl)ethylene.[11] Its further irradiation by visible light[12] in the presence of I_2 and air gave picene in 50-55% total yield. The reaction of picene with molten ferrocene in the presence of $AlCl_3$ and Al produced the binuclear iron complex $[(CpFe)_2(C_{22}H_{14})](PF_6)_2$ (**1**) in 54% yield (the use of molten ferrocene was originally proposed by Astruc and Saillard et al.).[9f] Noteworthy, attempts to prepare the mononuclear iron complex by conducting the same reaction with 1:1 ratio of reactants in decalin solvent or by substitution of naphthalene[13] in $[CpFe(C_{10}H_8)]PF_6$ were unsuccessful.

Complex **1** was obtained as a mixture of *cis*- and *trans*-isomers in ratio 1:9. Presumably, trans-isomer was a major product owing to the smaller electrostatic repulsion between cationic metal centers.[14] However, all single crystals obtained from this mixture contained only *cis*-**1** isomer as revealed by X-ray diffraction analysis. The iron atoms in **1** are coordinated to the terminal rings of picene in accordance with the general tendency observed for all polyarenes.[15] An interesting feature of the structure of *cis*-**1** is the twist of picene plane: the angle between the planes of the terminal C_6 rings reaches 12° (while free picene is almost flat).[16] Although the reason for this twist is not clear, we assume that it is partially caused by the crystal packing, because there is no such twist in the isolated structure of *cis*-**1,** that has been optimized by DFT methods.

Complex **1** is stable in air and well soluble in acetone and nitromethane. Irradiation of its solution by near-UV light (λ_{max}=365 nm, 36 Watt, 1 hour) led to precipitation of free picene, along with formation of ferrocene (detected by NMR) and iron salts. Treatment of filter paper with the solution of **1** and subsequent irradiation of the paper through a stencil produced a weakly fluorescent image due to formation of free picene. However, we could not produce thin films of picene on glass by this method because of its low adhesion.
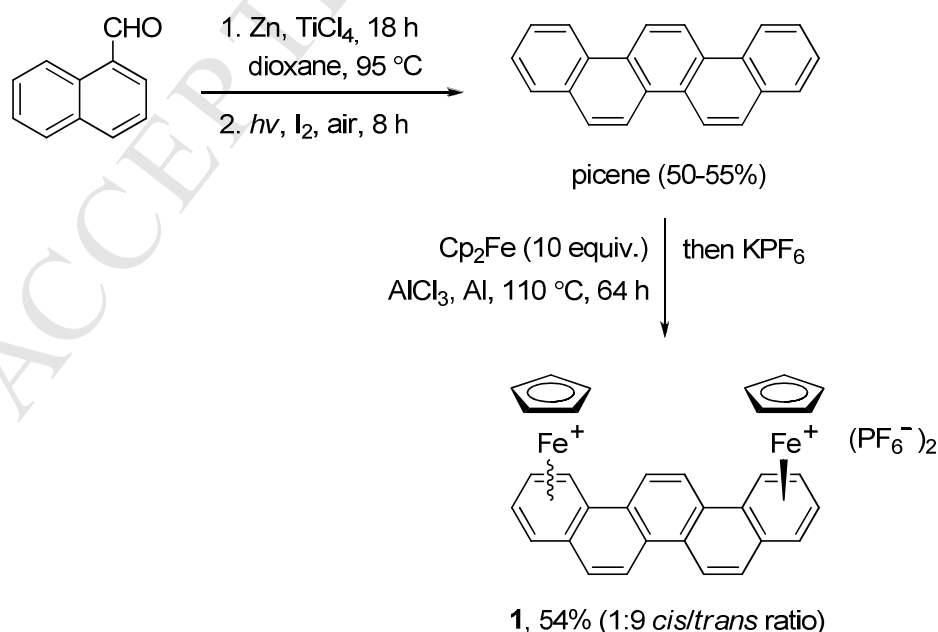
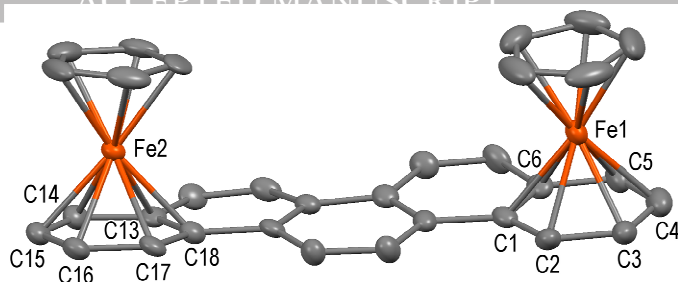Scheme 1. Synthesis of picene and its binuclear iron complex **1**.

Figure 1. The crystal structure of complex **1** in 50% thermal ellipsoids. Counter ions, solvate acetone molecule and all hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Fe1−C1 2.126(4), Fe1−C2 2.089(5), Fe1−C3 2.090(5), Fe1−C4 2.092(5), Fe1−C5 2.076(5), Fe1−C6 2.125(5), Fe2−C13 2.114(4), Fe2−C14 2.088(4), Fe2−C15 2.087(4), Fe2−C16 2.096(5), Fe2−C17 2.076(4), Fe2−C18 2.123(5), Fe1−Cp$_{plane}$ 1.674, Fe1−Cp$_{plane}$ 1.666.

The reaction of ruthenium precursor [Cp*Ru(MeCN)$_3$]PF$_6$ with picene in 1:1 ratio led to the mixture of mononuclear and binuclear complexes **2** and **3** (Scheme 3). The admixture of binuclear complex **3** was formed because picene is much less soluble than the intermediate mononuclear complex **2**. We managed to obtain pure mononuclear complex **2** by the reaction of [Cp*Ru(MeCN)$_3$]PF$_6$ with picene in the highly diluted solution with portion-wise addition of both reactants. Binuclear complex **3** was obtained in form of a mixture of cis- and trans-isomers by reaction of picene with 3 equivalents of [Cp*Ru(MeCN)$_3$]PF$_6$. The crystal structure of **2** was established by X-ray diffraction (Figure 2).
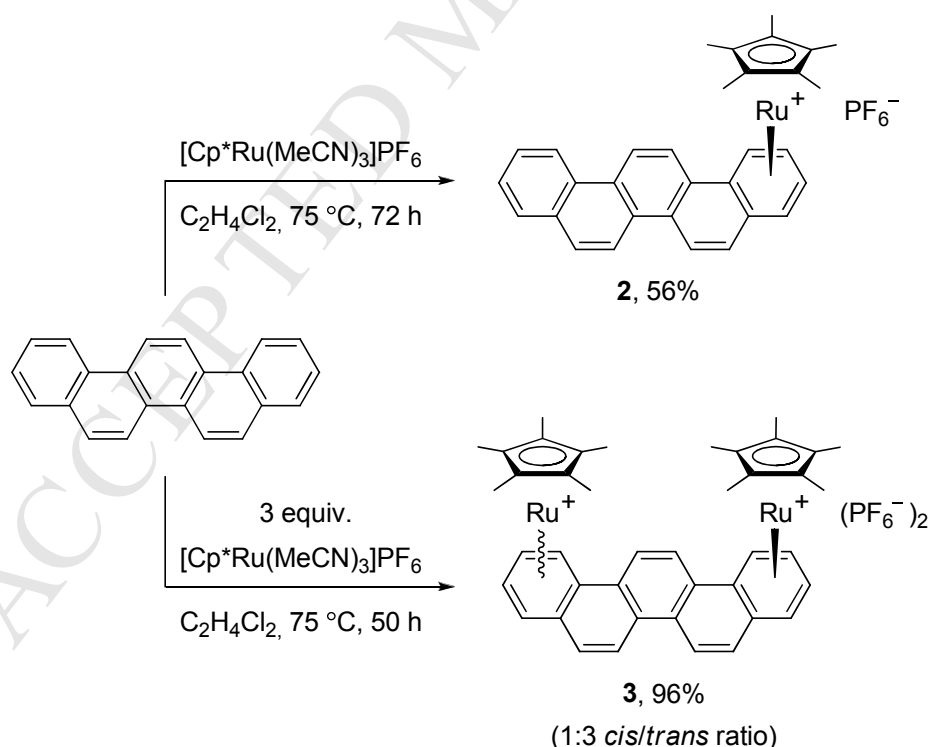
Scheme 2. Synthesis of ruthenium complexes of picene.

The coordination of ruthenium to picene in **2** is generally similar to its coordination to other polyarenes, for example, naphthalene.[17,18] In particular, one can notice characteristic elongation of bonds between ruthenium and bridgehead carbon atoms C1 and C6 (av. 2.268 Å) as compared to other Ru−C$_{picene}$ bonds

(av. 2.226 Å). We were unable to obtain suitable crystals for the X-ray diffraction analysis of dinuclear complexes **3** and therefore their structure were deduced from the NMR spectra and elemental analysis. The integration of ^{1}H NMR signals of picene and Cp* ligands clearly showed the attachment of two [Cp*Ru][+] fragments to the arene. For each of the isomers of **3** the number of the signals of picene in ^{1}H and ^{13}C NMR remained the same as in the free ligand, which indicated C_s or C_2 symmetry of the molecules (for *cis-* and *trans-*isomers of the complex, respectively). The signals of eight protons of picene were characteristically shifted upfield for ca. 0.5–1 ppm, which indicated coordination of metals to the terminal rings (coordination to the central rings would result in a shift of signals of only four protons). It is also noteworthy, that the spectral features of **3** were similar to the related dinuclear ruthenium complex of chrysene, which has been characterized by the X-ray diffraction.[19]
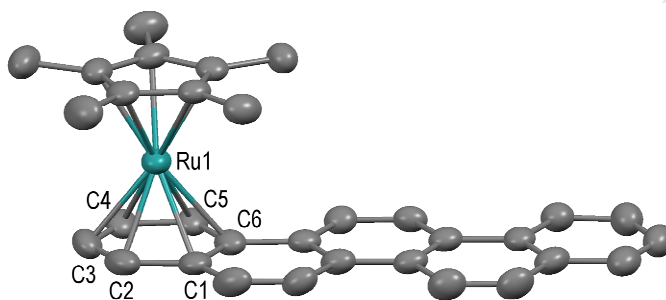

Figure 2. The crystal structure of complex **2** in 50% thermal ellipsoids. Counter ion, solvate benzene molecule and all hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru1–C1 2.259(5), Ru1–C2 2.214(5), Ru1–C3 2.227(5), Ru1–C4 2.231(5), Ru1–C5 2.231(5), Ru1–C6 2.277(4), Ru1-Cp*$_{plane}$ 1.809.

3. Conclusion

To conclude, we developed a convenient method for preparation of polycyclic semiconducting arene picene and synthesized its first transition metal complexes. The iron complex [(CpFe)$_2$(picene)](PF$_6$)$_2$ (**1**) is soluble in polar solvents and under near-UV irradiation decomposes to produce insoluble free picene. Such conversion of insoluble polyarenes into soluble metal complexes and their further regeneration by irradiation may be helpful for purification and deposition of thin films of polyarenes, although further research is necessary to unfold this idea.

4. Experimental part

4.1. General

All reactions were carried out under argon atmosphere in anhydrous solvents, which were purified and dried using standard procedures. The isolation of products was carried out in air. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Avance 400 spectrometer at 20°C. The chemical shifts are reported relative to residual signals of the solvent (for CHCl$_3$: 7.26 ^{1}H, 77.16 ^{13}C; for (CD$_3$)$_2$CO: 2.05 ^{1}H, 29.84 ^{13}C; for CHD$_2$NO$_2$: 4.33 ^{1}H, 62.80 ^{13}C). The starting complex [Cp*Ru(MeCN)$_3$]PF$_6$ was synthesized according to the published procedure.[20] The copies of NMR spectra of the compounds are given as supplementary data.

4.1. Synthesis of 1,2-di(1-naphthyl)ethylene

1-naphthaldehyde (1.20 ml, 9.0 mmol) and $TiCl_4$ (1.50 ml, 14 mmol) were dissolved in 1,4-dioxane (50 ml) in a Schlenk vessel (150 ml). The yellow-orange mixture was cooled to 0°C by ice bath and the suspension of Zn dust (1.77 g, 27 mmol) in 1,4-dioxane (20 ml) was added by small portions. The resulting black mixture was stirred at 95°C for 18 hours. The reaction progress was controlled by TLC (PE/EA = 5:1, R_f = 0.80, intensive blue fluorescence). The reaction mixture was then cooled to room temperature, treated with 10% solution of Na_2CO_3 (50 ml) and the product was extracted with diethyl ether (5×25 ml). Combined organic fractions were washed with water (2×25 ml) and dried over anhydrous Na_2SO_4. After evaporation of solution and drying in vacuum the light grey solid product was obtained (1.16 g, 92% yield, mixture of *cis-* and *trans-*isomers in 1:8 ratio). The product is pure enough for further synthesis.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, $^3J_{H-H}$ = 7.5 Hz, $2H_{trans}$), 8.20 (d, $^3J_{H-H}$ = 8.2 Hz, $2H_{cis}$), 7.94-7.85 (m, $8H_E$, $4H_{cis}$), 7.67 (d, $^3J_{H-H}$ = 7.7 Hz, $2H_{cis}$), 7.58-7.52 (m, $6H_{trans}$, $4H_Z$), 7.42 (s, $2H_{cis}$), 7.13-7.08 (m, $2H_{cis}$). The spectrum is in accordance with literature data.[21]

4.2. Synthesis of picene

1,2-di(1-naphthyl)ethylene (1.00 g, 3.6 mmol) and iodine (0.15 g, 5.9 mmol) were dissolved in a mixture of ethyl acetate (50 ml) and benzene (75 ml) in a Schlenk tube (200 ml). The solution was irradiated for 8 hours by the high pressure mercury vapor lamp with a phosphor coated bulb (Philips HPL-N 400W), which produced mostly visible light. During the irradiation, air was bubbled through the solution via a thin glass tube. Gradual formation of white crystals of the product was observed. After 8 hours, the precipitate was collected by filtration and washed with small portions of ethyl acetate until the discoloration of the filtrate. Drying in vacuum gave white crystals of picene (560 mg, 57% yield).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.97 (s, 2H), 8.87 (d, ^3J = 7.3 Hz, 2H), 8.80 (d, ^3J = 9.7 Hz, 2H), 8.06-8.01 (m, 4H), 7.75 (t, ^3J = 7.6 Hz, 2H), 7.67 (t, ^3J = 7.6 Hz, 2H). The spectrum is in accordance with literature data.[22]

*4.3. Synthesis of the complex [(CpFe)$_2$(C$_{22}$H$_{14}$)](PF$_6$)$_2$ (**1**)*

Ferrocene (1.86 g, 10 mmol), Al powder (54 mg, 2 mmol), anhydrous powdered $AlCl_3$ (1.335 g, 10 mmol) and picene (278 mg, 1 mmol) were placed in a Schlenk tube (25 ml) and mixed well with a spatula. The tube was covered with aluminum foil to prevent photochemical decomposition of the product. The mixture was heated for 64 hours at 110 °C, then cooled and triturated with several portions of diethyl ether under argon in order to remove unreacted ferrocene and $AlCl_3$. The residue was dried in a vacuum to give a grey powder. Then it was opened to air, hydrolyzed with water and the mixture was filtered through a short layer of Al_2O_3. The obtained yellow filtrate was treated with the solution of KPF_6 (368 mg, 2 mmol) in 10 ml of water and the yellow precipitate formed was collected by filtration. The precipitate was dissolved in a minimum amount of 1:1 mixture of CH_2Cl_2/CH_3NO_2 and the solution was dried over anhydrous Na_2SO_4. The solution was added in portions (400 μL) to the excess of diethyl ether (10 ml for each portion) to give orange precipitate of the product, which was then collected and dried in vacuum. The yield was 441 mg (54%). The NMR spectra revealed the presence of *cis-* and *trans-*isomers in 1:9 ratio.

^1H NMR (400 MHz, $(CD_3)_2CO$):

Major isomer (presumably *trans*): δ = 9.16 (s, 2H), 9.02 (d, ^3J = 9.4 Hz, 2H), 8.16-8.10 (m, 4H), 7.35 (d, ^3J = 4.0 Hz, 2H), 6.70 (m appear as s, 4H of the coordinated ring), 4.71 (s, 10H, Cp).

Minor isomer (presumably *cis*): δ = 9.37 (s, 2H), 9.20-9.16 (m, 2H), 8.34-8.25 (m, 4H), 7.50 (d, ^3J = 5.7 Hz, 2H), 6.83-6.80 (m, 4H of the coordinated ring), 4.81 (s, 10H, Cp).

^{13}C NMR (151 MHz, $(CD_3)_2CO$): after recrystallization – only one isomer is detected: δ = 131.84, 131.04, 129.42, 128.77, 125.60, 94.95, 93.75, 88.64, 88.05, 86.95, 82.15, 78.14 (Cp).

Elemental analysis (for crystals grown by slow diffusion of Et_2O vapors into solution of complex in nitromethane). Calculated for $C_{32}H_{24}F_{12}Fe_2P_2 \cdot CH_3NO_2$: C, 45.50; H, 3.12; N, 1.61. Found: C, 45.91.; H, 3.09; N, 1.09.

4.4. Synthesis of the complex [Cp*Ru(C22H14)]PF6 (2)

The mixture of 1,2-dichloroethane (20 ml) and acetonitrile (0.2 ml) was heated to 60°C in a Schlenk tube (50 ml) under argon atmosphere. Then picene (5.6 mg, 0.020 mmol) was added and the mixture was vigorously stirred for 1 hour until complete dissolution of ligand. After that [Cp*Ru(MeCN)₃]PF₆ (10 mg, 0.020 mmol) was added to resulting solution and the mixture was stirred for additional 30 minutes. This procedure (picene dissolution and complex addition) was repeated 3 times more. Then the reaction mixture was heated up to 75°C and stirred for 3 days. The resulting brown solution was opened to air and evaporated to dryness. The residue was dissolved in a small amount of nitromethane and the solution was filtered through a short column (~5 cm layer of Al_2O_3 in Pasteur pipette). The solution was evaporated to a minimum amount (ca 0.5 ml) and added to the excess of Et_2O to precipitate the light grey product, which was dried in vacuum. The yield was 29 mg (56% yield).

^{1}H NMR (400 MHz, CD_3NO_2): δ = 8.98 (d, ^3J = 9.1 Hz, 1H), 8.84 (d, ^3J = 9.6 Hz, 1H), 8.80 (d, ^3J = 8.0 Hz, 1H), 8.62 (d, ^3J = 9.2 Hz, 1H), 8.47 (d, ^3J = 9.0 Hz, 1H), 8.03 (d, ^3J = 9.2 Hz, 1H), 8.00 (d, ^3J =7.6 Hz, 1H), 7.76 (t, ^3J = 7.0 Hz, 1H), 7.71 (t, ^3J = 7.3 Hz, 1H), 7.48 (d, ^3J = 9.5 Hz, 1H), 7.12 (d, ^3J = 6.2 Hz, 1H of the coordinated ring), 6.43-6.37 (m, 1H of the coordinated ring), 6.10-5.96 (m, 2H of the coordinated ring), 1.40 (s, 15H, Cp*).

^{13}C NMR (101 MHz, CD_3NO_2): δ = 133.87, 131.86, 131.43, 131.26, 130.36, 130.31, 129.99, 129.44, 129.20, 128.78, 127.71, 126.29, 125.44, 124.88, 123.10, 122.59, 96.21 ($\underline{C}_5Me_5$), 96.13, 95.24, 89.63, 89.35, 87.41, 82.10, 9.95 ($C_5\underline{Me}_5$).

Elemental analysis (for crystals grown by slow diffusion of C_6H_6 vapors into the solution of complex in $(CH_3)_2CO$). Calculated for $C_{32}H_{29}F_6PRu$: C, 58.27; H, 4.43. Found: C, 57.71; H, 4.50.

4.5. Synthesis of the complex [(Cp*Ru)2(C22H14)](PF6)2 (3)

A mixture of [Cp*Ru(MeCN)₃]PF₆ (76 mg, 0.15 mmol) and picene (14 mg, 0.05 mmol) in 1,2-dichloroethane (2.5 ml) was stirred at 75°C for 50 hours. The mixture was then opened to air and evaporated The residue was dissolved in a small amount of nitromethane and the solution was filtered through a short column (~5 cm layer of Al_2O_3 in Pasteur pipette). The solution was evaporated to a minimum amount (ca 0.5 ml) and added to the excess of Et_2O to precipitate the grey solid. It was

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washed with CH_2Cl_2 (2 ml) and dried in vacuum to give the product (50 mg, 96% yield). The NMR spectra revealed the presence of *cis*- and *trans*-isomers in 1:3 ratio.

^{1}H NMR (400 MHz, CD_3NO_2):

Major isomer (presumably *trans*): δ = 8.95 (d, ^3J = 9.6 Hz, 2H), 8.86 (s, 2H), 7.72 (d, ^3J = 9.6 Hz, 2H), 7.38-7.36 (m, 2H of the coordinated ring), 6.63-6.62 (m, 2H of the coordinated ring), 6.26-6.24 (m, 4H of the coordinated ring), 1.56 (s, 30H, Cp*).

Minor isomer (presumably *cis*): δ = 8.87 (d, ^3J = 7.5 Hz, 2H), 8.77 (s, 2H), 7.67 (d, ^3J = 9.6 Hz, 2H), 7.31-7.30 (m, 2H of the coordinated ring), 6.58-6.56 (m, 2H of the coordinated ring), 6.22-6.20 (m, 4H of the coordinated ring), 1.56 (s, 30H, Cp*).

^{13}C NMR (101 MHz, CD_3NO_2):

Major isomer (presumably *trans*): δ = 131.89, 130.71, 128.42, 127.86, 125.92, 97.08 ($\underline{C}_5Me_5$), 96.55, 94.98, 90.35, 89.96, 87.97, 82.71, 10.12 ($C_5\underline{Me}_5$).

Minor isomer (presumably *cis*): δ = 131.50, 130.23, 128.16, 127.90, 125.82, 96.85 ($\underline{C}_5Me_5$), 96.18, 94.70, 90.35, 89.87, 87.80, 82.44, 10.17 ($C_5\underline{Me}_5$).

Elemental analysis (for crystals grown by slow diffusion of Et_2O vapors into the solution of complex in CH_3NO_2). Calculated for $C_{42}H_{44}F_{12}P_2Ru_2$: C, 48.46; H, 4.26. Found: C, 48.01; H, 4.59.

4.6. X-ray crystallography

Crystals of **1** ($C_{33.50}H_{27}F_{12}Fe_2O_{0.5}P_2$, M = 839.19) are triclinic, space group P-1, at 120 K: a = 7.2106(18), b = 14.686(4), c = 15.053(4) Å, α = 81.363(6), β = 87.375(6), γ = 84.815(6)°, V = 1568.7(7) Å^3, Z = 2, d_{calc} = 1.777 gcm^{-3}, μ(MoKα) = 11.27 cm^{-1}, F(000) = 844. Crystals of **2** ($C_{38}H_{35}F_6PRu$, M = 737.70) are triclinic, space group P-1, at 120 K: a = 10.6080(19), b = 11.464(2), c = 14.269(3) Å, α = 104.808(3), β = 107.610(3), γ = 92.942(3)°, V = 1583.2(5) Å^3, Z = 2 (Z' = 1), d_{calc} = 1.547 gcm^{-3}, μ(MoKα) = 6.09 cm^{-1}, F(000) = 752. Intensities of 16591 and 21121 reflections for **1** and **2**, respectively, were measured with a Bruker APEX2 DUO CCD diffractometer [λ(MoKα) = 0.71072Å, ω-scans, 2θ<54°]; 6792 and 6927 independent reflections were used in further refinement. The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. For **1**, the refinement converged to wR2 = 0.1333 and GOF = 1.001 for all the independent reflections (R1 = 0.0599 was calculated against F for 4116 observed reflections with I>2σ(I))**.** For **2**, the refinement converged to wR2 = 0.1717 and GOF = 1.077; R1 = 0.0598 was calculated against F for 5006 observed reflections**.** All calculations were performed using SHELXTL PLUS 5.0 [23]. CCDC 1855100 and 1855101 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
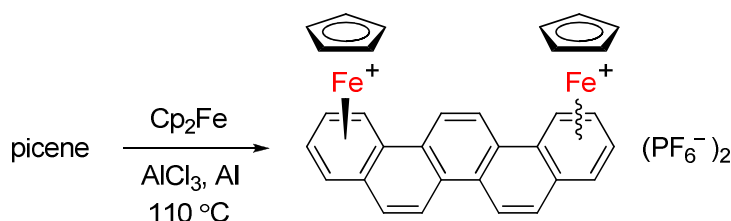
Appendix A. Supplementary data

Copies of NMR spectra for the picene and its complexes. The optimized structures of *cis*- and *trans*-isomers of the iron complex **1**.

Graphical abstract

Highlights

Semiconducting aromatic hydrocarbon picene $C_{22}H_{14}$ was synthesized from 1-naphthaldehyde

The first iron and ruthenium complexes of picene were synthesized and studied by X-ray diffraction

Metal coordination can help to increases solubility of polyarenes

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