Tetra(hetero)arylated Cyclopentadienone Iron Tricarbonyl Complexes for Noble Metal-free Photocatalytic Hydrogen Generation

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Abstract

A versatile method for the straightforward synthesis of rarely known tetra(hetero)arylated cyclopentadienone iron tricarbonyl complexes **3a**-**3j** is presented. In a [2+2+1]-cycloaddition reaction, a series of di(hetero)arylated ethynylenes **1a**-**1j** are reacted with iron pentacarbonyl to yield the corresponding "Knölker-type" complexes, which bear substituents of different electronic nature. This type of iron complexes is active in photocatalytic hydrogen evolution reaction and the influence of the substituents on the catalytic activity was investigated.

Introduction

Photocatalytic hydrogen evolution reaction (HER) combines straightforward renewable solar energy conversion and concurrent storage in chemical binding energy. Typically, a combination of photosensitizer (PS) as light harvester and catalyst (Cat) is necessary for the direct conversion of light into hydrogen.[1] However, most homogeneous PS-Cat systems rely on expensive precious metals such as Rh, Pd, Ru, or Ir. Therefore, it is highly attractive to replace them by non-precious, noble metal-free, and abundant metals such as iron.[2] Despite molecularly defined iron catalysts typically involve one-electron transfer processes as homogeneous catalysts, binuclear [FeFe]-hydrogenase mimics, which consist of a bridged system between an organic PS and an iron complex catalyst, showed impressive photocatalytic activities in HER by managing the two-electron process for the reduction of protons to hydrogen.[3]

Alternatively, bifunctional metal-ligand catalysts such as mononuclear Fe-complexes with 'non-innocent' ligands have been developed.[4] Already in 1953, Reppe and Vetter investigated the influence of iron pentacarbonyl [Fe(CO)$_5$] on olefins and ethynylenes under different conditions. The formation of various iron complexes was observed for ethynylenes.[5] The first structural elucidation was managed by Schrauzer by reacting tolane (diphenylethynylene) with iron carbonyls such as Fe$_3$(CO)$_{12}$ or Fe$_2$(CO)$_9$ at elevated temperature in benzene to give 2,3,4,5-tetraphenylcyclopentadienone (CPD) iron tricarbonyl, which represented the first member of a complex, in which a CPD is bonded via π-electrons to a transition metal.[6] Independently, the research groups of Knölker and Pearson later on intensively studied the [2+2+1]-cycloaddition of alkynes and carbon monoxide and the resulting iron complexes.[7] The stability of the CPDs was significantly enhanced by complexation with iron and the in-

troduction of stabilizing residues on the ring. Subsequently, various monocyclic and bicyclic CPD iron complexes with different residues were prepared and characterized. The complexes proved to be stable to water and air and can be stored under ambient conditions for extended periods of time. Moreover, the electrochemical properties can be controlled by the introduction of electron-pushing or electron-withdrawing substituents on the CPD.[7b-d] More specifically, the redox active bicyclic cyclopentadienone iron tricarbonyl (CPD-FeCO$_3$) "Knölker-type" complexes exhibited substantial catalytic activity, which was influenced by the substituents at the CPD ring as well on the Fe-center, and were successfully used in (asymmetric) catalytic hydrogenation/dehydrogenation reactions, alkylations, and in energy-related transformations.[8]

In the latter application, Beller et al. developed the use of *in-situ* generated "Knölker-complexes" as photocatalyst in a completely noble metal-free HER-system due to their good stability against water and air.[9] In conjunction with a copper(I)-based PS, hydroxide as base, triethylamine (TEA) as sacrificial electron donor, THF-water mixture as hydrogen source, and irradiation with a Xe-lamp as light source, various investigated CPD-FeCO$_3$ catalysts after optimization delivered significantly higher activities compared to the originally used Fe$_3$(CO$_{12}$)-catalyst.[10] Turn-over numbers (TON) of up to 131 were achieved.

In the course of our work on cyclopentadienone derivatives for regenerative energy applications,[11] we herein report straightforward and versatile synthesis of rarely known tetra-(hetero)arylated CPD-FeCO$_3$ complexes and their performance in photocatalytic HER. The variation of the electronic nature of the (hetero)aryl substituents at the CPD-core gives insight into structure-property relationships in this class of catalytically active mononuclear Fe-complexes.

Results and Discussion

Synthesis. The synthesis of 2,3,4,5-tetraphenylcyclopentadienone-FeCO$_3$ complex **3a** was described in earlier reports and typically was prepared by reaction of tetracyclone and iron carbonyls.[6,12] The catalytic activity of **3a** and related complexes was tested for transfer hydrogenation of carbonyl compounds to alcohols and corresponding oxidation of alcohols to aldehydes and ketones. In both type of reactions, arylated complexes exhibited higher reactivity than that of bicyclic Knölker complexes.[9b] With respect to HER, Beller et al. showed

that tetraphenylated CPD-FeCO$_3$ complex **3a** was catalytically active with TON of up to 65 which is smaller compared to the Knölker-type complexes under identical conditions (TON ≤ 78, vide supra).[9] Therefore, we chose complex **3a** as a reference system for our investigations.

In order to straightforwardly synthesize tetra(hetero)arylated CPD-FeCO$_3$ complexes with different electronic properties, we reacted di(hetero)arylated ethynylenes **1a-j** with an excess of iron pentacarbonyl (FeCO$_5$) in toluene at temperatures of 110-130 °C in a [2+2+1]-cycloaddition to result in **3a** and a series of novel CPD-FeCO$_3$ complexes **3b-j** in moderate to excellent yields. In order to obtain structure-property relationships, the substituents at the CPD-core were varied from electron-rich (bi)thiophenes (**3b-f**) to phenyl (**3a**), donor or acceptor-substituted phenyls (**3g-i**), and to electron-deficient pyrimidine (**3j**) (Scheme 1). The structures of the novel CPD-FeCO$_3$ complexes **3b-j** were characterized by NMR and IR-spectroscopy. NMR spectra were in accordance with the proposed structures and particularly in the ^{13}C spectra, the iron bound carbonyls are observed at 214-203 ppm, the CPD carbonyl group between 171-162 ppm. In the IR spectra for both type of carbonyl strong absorption peaks were seen in the range of 2076-1949 cm^{-1} for the iron carbonyls and 1697-1600 cm^{-1} for the central CPD moiety. The symmetrically substituted ethynylenes **1a-j** were either obtained commercially, prepared according to literature procedures, or newly synthesized.
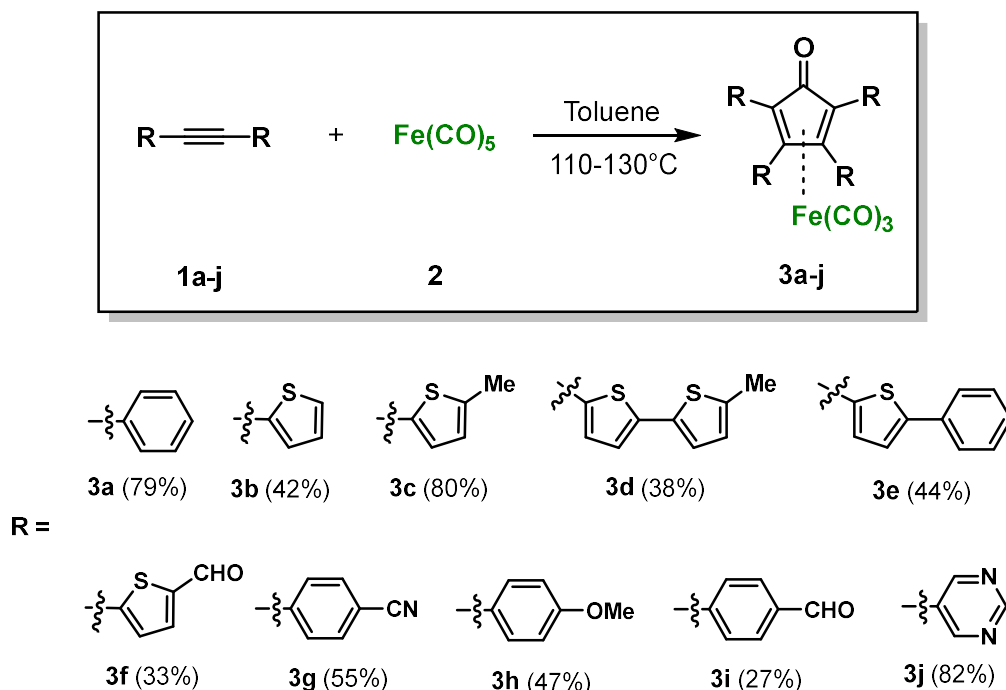
Scheme 1. Synthesis of tetra(hetero)arylated (cyclopentadienone)iron tricarbonyl complexes **3a-j**.

4

Light-driven hydrogen evolution reaction of (cyclopentadienone)iron tricarbonyl complexes 3a, 3c, 3g, 3h, 3i, and 3j. In order to compare the catalytic activity of the selected newly synthesized CPD-FeCO$_3$ complexes **3c**, **3g**, **3h**, **3i**, and **3j** in HER with tetracyclone-FeCO$_3$ complex **3a** (Scheme 2), investigations were performed under similar conditions as those recently applied by Beller et al.[9] In this respect, heteroleptic copper(I) complex [Cu(Xantphos)(bathocuproine)PF$_6$] (CuPS) served as PS, TEA as sacrificial donor in a THF-water mixture, and tetraethylammonium hydroxide was added as base to activate the iron complex. The solution was irradiated at 25 °C with a Xenon lamp as light source and gas analysis was performed by gas chromatography with thermal conductivity detector.
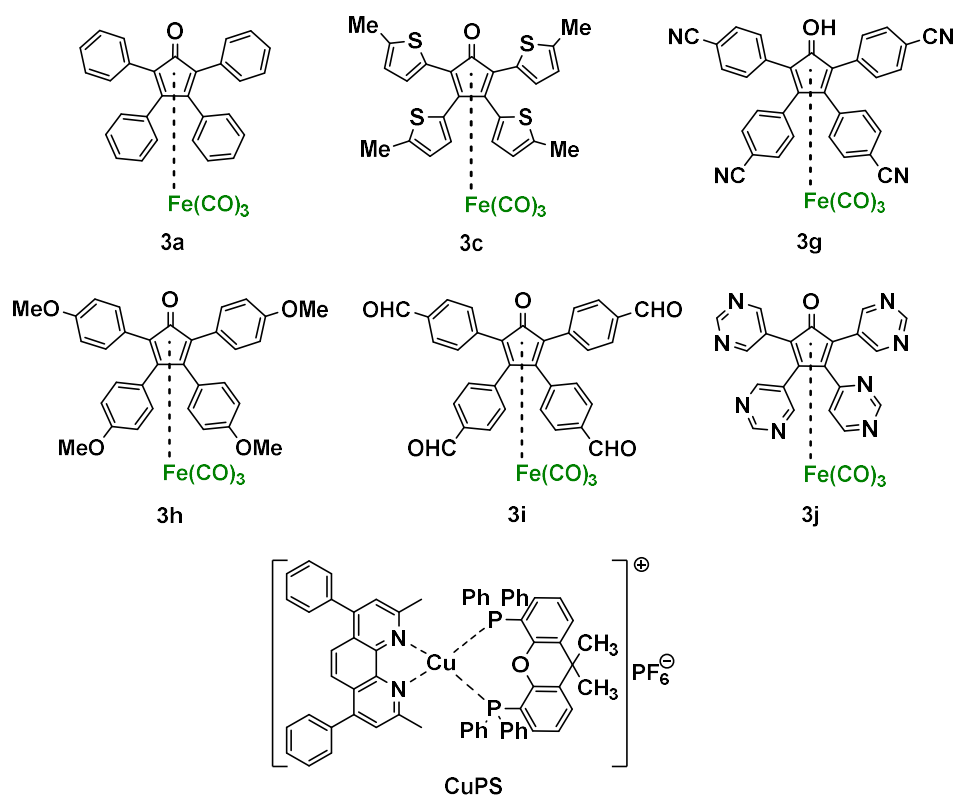
Scheme 2. 2,3,4,5-Tetra(hetero)arylated cyclopentadienone iron tricarbonyl complexes **3a**, **3c**, **3g**, **3h**, **3i**, and **3j** investigated as HER-catalyst in conjunction with photosensitizer CuPS..

The results of the measurements after 8 hours and at the end of each experiment (24 hrs) are summarized in Table 1 and shown in Figure 1 as a plot of TON and quantity of hydrogen versus the illumination time. After 8 hrs of irradiation the benzonitrile CPD-FeCO$_3$ complex **3g** showed the highest catalytic activity in the series (TON = 155) and outperformed reference complex phenyl CPD **3a** (TON = 79). In the series phenyl CPD derivatives, the TON is

steadily increasing when going from donor-substituted **3h** (TON = 59) to phenyl **3a** and to best performing acceptor-substituted **3g** and decreases again for more electron-deficient benzaldehyde CPD-FeCO₃ complex **3i** (TON = 50). The heteroarylated complexes **3c** (TON = 59) and **3j** (TON = 62) were as well relatively moderately efficient, whereby thiophene-based complex **3c** partially decomposed after prolonged illumination. The same overall trend is observed after driving HER to 24 hrs and benzonitrile CPD-FeCO₃ complex **3g** reached the highest TON of 253.

Table 1. Results of the photocatalytic hydrogen evolution reaction with (cyclopentadienone)iron tricarbonyl complexes **3a**, **3c**, **3g**, **3h**, **3i**, and **3j**, their reduction potentials vs Fc/Fc⁺ and LUMO energy levels in comparison to CuPS.

Cat.	R	time [h]	H₂ [μmol]	TON	time [h]	H₂ [μmol]	TON	E_p^{Red} [V]	LUMO [eV]
3h	Ph-OMe	8	70	59	24	135	114	-2.11	-3.31
3c	Th-Me	8	70	59	24	50	42	-1.92	-3.41
3a	Ph	8	93	79	24	202	171	-1.83	-3.49
3g	**Ph-CN**	**8**	**183**	**155**	**24**	**299**	**253**	**-1.75**	**-3.62**
3i	Ph-CHO	8	59	50	24	181	153	-1.46	-3.80
3j	Pyrimidine	8	73	62	24	171	145	-1.38	-3.91
CuPS								-2.04	-3.17

Reaction conditions: CuPS (3.65 μmol), catalyst (1.18 μmol), Et₄NOH (12 μmol), THF/TEA/H₂O (4:3:1, 10 mL), r.t., Xe-light irradiation (output 1 W), without light filter, gas evolution quantitatively measured by gas syringe, gas analysis by GC. All values are the average of three experiments. Cyclic voltammograms in acetonitrile, tetrabutylammonium tetrafluoroborate (0.1 M), scan speed 100 mV/s, r.t., potentials vs ferrocene/ferricenium (Fc/Fc+). LUMO energies calculated from the onset values of the first reduction wave; Fc/Fc⁺ was set to -5.1 eV vs. vacuum (E_{LUMO}=-5.1 eV-E_{on}^{Red1}).
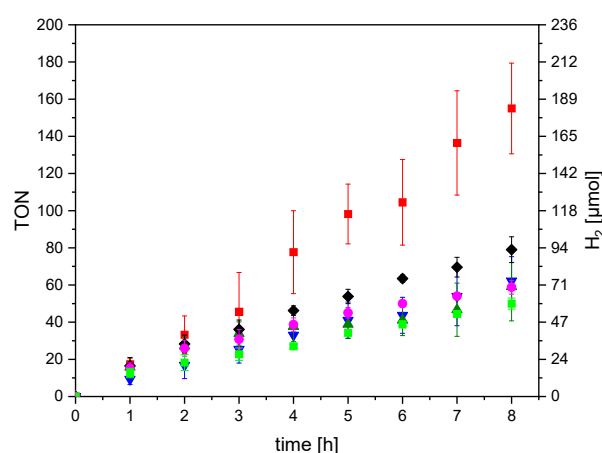

Figure 1. Photocatalytic hydrogen evolution of CPD-Fe-complexes **3a** (black curve), **3c** (dark green), **3g** (red), **3h** (pink), **3i** (light green), and **3j** (blue). Experimental details: CuPS (3.65 μmol), Fe-catalyst (1.18 μmol), Et₄NOH (12 μmol), THF/TEA/H₂O (4:3:1, 10 mL), r.t., Xe-light irradiation (output 1 W), without light filter, gas evolution quantitatively measured by gas syringe, gas analysis by GC. All values are the average of three experiments.

The mechanism of HER including these mononuclear Fe-complexes with 'non-innocent' ligands is well investigated and comprises reduction of an intermediate hydrido iron complex by electron transfer from the reduced PS under release of hydrogen.[9] Therefore, the reduction potential of the iron complex and corresponding LUMO energy might play a role in the efficiency of electron transfer and consequently catalytic activity. In this context, we investigated the redox properties of the iron complexes and CuPS by cyclic voltammetry in acetonitrile and tetrabutylammonium tetrafluoroborate (0.1 M) as electrolyte. The potentials were referenced against the ferrocene/ferricenium couple (Fc/Fc$^+$) and LUMO energy levels were calculated from the onset values of the first reduction wave (Table 1). In general, the CPD-FeCO$_3$ complexes showed irreversible reduction (and oxidation) waves. We address this redox process to the reduction of the central CPD unit and the formation of instable radical anions which is influenced by the electronic character of the four (hetero)aromatic substituents. In this respect, the reduction potential is successively shifted positive when going from CPD-FeCO$_3$ complex **3h**, which due to the electron-rich *p*-methoxyphenyl substituents was most difficult to reduce and showed the most negative reduction potential (E_p^{Red} = -2.11 V), to finally the most electron-deficient pyrimidine-based complex **3j** (E_p^{Red} = -1.38 V). Consequently, the LUMO energy levels become more negative in this sequence and range from -3.31 eV for **3h** to -3.91 eV for **3j**. Therefore, it is obvious that electron transfer from the reduced CuPS is guaranteed for all six complexes and contributes to their catalytic activity, because the LUMO energy level of CuPS (E_{LUMO} = -3.17 eV) is higher than those of all complexes. At first glance, the efficiency of HER (**3h** ≤ **3c** < **3a** < **3g**) roughly correlates with the lowering of the reduction potentials and LUMO energy levels in the series due to increasing electron-accepting character of the substituents at the CPD-core. However, for the even more electron-deficient derivatives, benzaldehyde **3i** and pyrimidine-CPD-FeCO$_3$ complex **3j** reduced activity in HER is noted which we address to other factors playing a role in the catalytic cycle. Therefore, the electronic properties of benzonitrile CPD-FeCO$_3$ complex **3g** seem to be optimal for HER under these conditions (Table 1).

Conclusion

In summary, we have developed a straightforward and versatile synthesis for rarely known tetra(hetero)arylated cyclopentadienone iron tricarbonyl complexes **3a**-**3j** and investigated

their photocatalytic activity in hydrogen evolution reaction. Thereby, *p*-cyanophenyl-substituted CPD-complex **3g** yielded the best performance in the series with a TON of 253 after 24 hours surpassing the known tetraphenyl derivative **3a**. The variation of the electronic nature of the fourfold (hetero)aryl substituents at the CPD-core gave insight into structure-property relationships and a rough correlation of the reduction behaviour and LUMO energies with HER-activity was obtained.

Experimental Section

Instruments and measurements. NMR spectra were recorded on an Avance 400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 101 MHz) or a Bruker AMX 500 spectrometer (^{1}H NMR: 500 MHz, ^{13}C NMR: 125 MHz). Chemical shifts (δ) are reported in ppm using residual solvent protons (^{1}H NMR: δ_H = 7.26 for CDCl$_3$; δ_H = 3.58 and 1.72 for THF-d_8; ^{13}C NMR: δ_C = 77.16 for CDCl$_3$; δ_C = 67.21 and 25.31 for THF-d_8) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constants *J* relate to proton-proton couplings. Thin layer chromatography was carried out on aluminum plates, precoated with silica gel, Merck Si60 F254. Preparative column chromatography was performed on glass columns packed with silica gel (particle size 40–63 μm) from Macherey-Nagel. Melting points were determined using a Büchi Melting Point B-545 (not corrected). High resolution MALDI mass spectra were performed on a Bruker SolariX using trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. High resolution ESI mass spectra were performed on a Bruker SolariX using acetonitrile as solvent. IR spectroscopy was performed with a Bruker Alpha II FT-IR spectrometer and elemental analyses with an Euro Vector EA3000 Element Analyser.

Cyclic voltammetry experiments were performed with a computer-controlled Autolab PGSTAT30 potentiostat in a three-electrode single-compartment cell (3 mL). The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of A = 0.785 mm^2, which was polished down to 0.25 μm with Buehler polishing paste prior to use to guarantee reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was an Ag/AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferricenium couple (Fc/Fc$^+$). For the measurements, concentrations of 10^{-3} M of the electroactive species were used in freshly distilled and deaerated acetoni-

trile and tetrahydrofuran (Sigma Aldrich) purified with a Braun MB-SPS-800 and 0.1 M (n-Bu)$_4$NBF$_4$ (Fluka; recrystallized twice from ethanol).

Materials and synthesis of ethynylenes 1b-1j. Toluene (Sigma Aldrich), tetrahydrofuran (THF) (Carl Roth GmbH) were dried and purified by a MB SPS-800 (MBraun). Dichloromethane, ethyl acetate, diethyl ether and petroleum ether and were purchased from VWR. Tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$dba$_3$), tri-*tert*-butylphosphonium tetrafluoroborate, potassium carbonate, phenylboronic acid, iron pentacarbonyl, triethylamine (TEA), tetraethylammonium hydroxide (Et$_4$NOH), THF-d$_8$, and CDCl$_3$ were purchased from Sigma Aldrich, magnesium sulfate from Grüssing GmbH and silica gel from Macherey-Nagel.

1,2-Diphenylethynylene (tolane) **1a** was purchased from Sigma Aldrich. The following ethynylene derivatives and intermediates were synthesized according to literature-known procedures: 1,2-bis(2-thienyl)ethynylene **1b**,[13] 1,2-bis(5-methylthien-2-yl)ethynylene **1c**,[14] 1,2-bis(5-formylthien-2-yl)ethynylene **1f**,[15] 1,2-bis(*p*-cyanophenyl)ethynylene **1g**,[16] 1,2-bis(*p*-methoxyphenyl)ethynylene **1h**,[17] 1,2-bis(*p*-formylphenyl)ethynylene **1i**,[18] 1,2-bis(pyrimid-5-yl)ethynylene **1j**,[19] 1,2-bis(5-bromothien-2-yl)ethynylene **1k**,[20] (bathocuproin)(xantphos)-copper(I)hexafluorophosphate (CuPS),[21] Pd[PPh$_3$]$_4$,[22] and 4,4,5,5-tetramethyl-2-(5-methyl-2-thienyl)-1,3,2-dioxaborolane[23] were synthesized according to a literature-known procedures.

1,2-Bis(5'-methyl-5,2'-bithien-2-yl)ethynylene (1d): 1,2-Bis(5-bromothien-2-yl)ethynylene **1k** (100 mg, 0.29 mmol), 4,4,5,5-tetramethyl-2-(5-methyl-2-thienyl)-1,3,2-dioxaborolane (154 mg, 0.69 mmol), Pd$_2$dba$_3$ (26 mg, 0.03 mmol), and tri-*tert*-butylphosphonium tetrafluoroborate (13 mg, 0.05 mmol) were dissolved in dry THF (10 mL) and purged with argon. Then, potassium carbonate (480 mg, 3.47 mmol) was dissolved in water (5 mL), added, and the reaction mixture heated at 60 °C for 72 h. For work-up, diethyl ether was added to the mixture and washed with water. The aqueous phase was counter-shaken twice with diethyl ether. After drying the organic phase over magnesium sulfate and removing the solvent, column chromatography was performed (silica gel SiO$_2$), petroleum ether (PE)/dichloromethane (DCM) 3:1. 1,2-Bis(5'-methyl-5,2'-bithien-2-yl)ethynylene **1d** (88 mg, 0.23 mmol, 80%) was obtained as a yellow solid. Mp 209-212 °C; ^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.14 (d, ^3J=3.8 Hz, 2 H, *H-3*), 6.99 (d, ^3J=3.5 Hz, 2 H, *H-3'*), 6.97 (d, *J*=3.8 Hz, 2 H, *H-4*), 6.67 (dd, ^3J=3.5 Hz,

^4J=1.1 Hz, 2 H, *H-4'*), 2.49 (d, ^4J=1.1 Hz, 6 H, *CH₃*) ppm; ^{13}C-NMR (CDCl₃, 101 MHz): δ=140.2, 139.9, 134.5, 133.0, 126.3, 124.4, 123.0, 120.9, 87.4, 15.6 ppm. HR-MS (FTICR-MALDI): m/z= [M⁺], calcd. for $C_{20}H_{14}S_4$: 381.99729, found: 381.99659; *δm/m*=1.83 ppm.

1,2-Bis(5-phenylthien-2-yl)ethynylene (1e): 1,2-bis(5-bromothien-2-yl)ethynylene **1k** (500 mg, 1.44 mmol), phenylboronic acid (525 mg, 4.31 mmol). Pd₂dba₃ (132 mg, 0.14 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (66.7 mg, 0.23 mmol) were dissolved in dry THF (41 mL) and purged with argon. Then, potassium carbonate (2.38 g, 17.2 mmol) was dissolved in water (17 mL), added, and the reaction mixture heated at 60 °C for 72 h. For work-up, diethyl ether was added to the mixture and washed with water. The aqueous phase was counter-shaken twice with diethyl ether. After drying the organic phase over magnesium sulfate and removing the solvent, column chromatography was performed (SiO₂, PE/DCM 9:1). 1,2-Bis(5-phenylthien-2-yl)ethynylene **1e** (209 mg, 0.61 mmol, 42%) was obtained as a yellow solid. Mp 210-214 °C; ^{1}H-NMR (CDCl₃, 400 MHz): δ=7.60 (d, ^3J=7.4 Hz, 4 H, *H-2'*), 7.40 (t, ^3J=7.6 Hz, 4 H, *H-3'*), 7.31 (t, ^3J=7.4 Hz, 2 H, *H-4'*), 7.26 (d, ^3J=3.8 Hz, 2 H, *H-3*), 7.22 (d, ^3J=3.8 Hz, 2 H, *H-4*) ppm; ^{13}C-NMR (CDCl₃, 101 MHz): δ=146.9, 134.1, 133.9, 129.6, 128.7, 126.4, 123.9, 122.4, 87.6 ppm. HR-MS (FTICR-MALDI) calcd. for $C_{22}H_{14}S_2$: m/z= 342.05369, found: m/z=342.05252 [M⁺], *δm/m*=3.42 ppm.

General procedure for the synthesis of cyclopentadienon iron tricarbonyl complexes 3a-3j.
In a dried Schlenk tube, acetylenes **1a-1j** (1 eq) and iron pentacarbonyl (5 eqs) were dissolved in dry toluene. The reaction mixture was stirred at 90-130 °C for 3-31 d. The crude product was purified via column chromatography (LC) to yield corresponding cyclopentadienone iron tricarbonyl complexes.

[2,3,4,5-Tetraphenylcyclopentadienyl]iron tricarbonyl (3a): 1,2-diphenylethynylene **1a** (200 mg, 1.12 mmol), Fe(CO)₅ (0.75 mL, 5.61 mmol), toluene (10 mL); 130 °C for 10 d; LC: SiO₂, PE/ethyl acetate (EA) 1:1; CPD-FeCO₃ complex **3a** (233 mg, 0.44 mmol, 79%) was isolated as yellow solid. Mp >175 °C (decomp.); ^{1}H-NMR (400 MHz, THF-d₈) δ=7.69-7.64 (m, 4H, *Ph*), 7.30-7.27 (m, 4H, *Ph*), 7.23-7.13 (m, 12H, *Ph*) ppm; ^{13}C-NMR (101 MHz, THF-d₈) δ=210.3, 203.5, 171.4, 133.1, 131.7, 131.1, 129.5, 128.9, 128.7, 128.5, 105.7, 82.2 ppm; HR-MS (ESI+): calcd. for $C_{32}H_{20}FeO_4$: m/z=525.07837 [M+H]⁺, found: m/z=525.07834 [M+H]⁺; *δm/m*= 0.06

ppm; elemental analysis: calc. (%) for $C_{32}H_{20}FeO_4$: C 73.30, H 3.84; found: C 73.53, H 4.03; IR $\tilde{v}$ = 3056 (w), 2058 (vs), 2008 (vs), 1992 (vs), 1639 (vs), 1495 (m), 1443 (m), 1031 (m), 640 (m), 800 (m), 774 (m) cm^{-1}. The analytical data was in accordance with literature.[24]

[2,3,4,5-Tetra(thien-2-yl)cyclopentadienone]iron tricarbonyl (3b): 1,2-di(thien-2-yl)ethynylene **1b** (200 mg, 1.05 mmol), Fe(CO)$_5$ (0.71 mL, 5.26 mmol), toluene (6 mL); 90 °C for 31 d; LC: SiO$_2$, PE; CPD-FeCO$_3$ complex **3b** (120 mg, 0.22 mmol, 42%) was isolated as yellow solid. Mp >100 °C (decomp.); ^{1}H-NMR (400 MHz, THF-d$_8$) δ=7.28 (dd, ^3J=5.1 Hz, ^4J=1.2 Hz, 2 H, *H-5*), 7.18 (dd, ^3J=5.1 Hz, ^4J=1.2 Hz, 2 H, *H-5*), 6.85 (dd, ^3J=3.6 Hz, ^4J=1.2 Hz, 2 H, *H-3*), 6.80 (dd, ^3J=5.1 Hz, 3.6 Hz, 2 H, *H-4*), 6.76 (dd, ^3J=5.1 Hz, 3.6 Hz, 2 H, *H-4*), 6.75 (dd, ^3J=3.6 Hz, ^4J=1.2 Hz, 2 H, *H-3*) ppm; ^{13}C-NMR (101 MHz, THF-d$_8$) δ=213.9, 204.4, 163.0, 152.1, 136.8, 132.2, 129.6, 128.8, 127.5, 127.2, 127.1, 126.2 ppm; IR $\tilde{v}$ = 3102 (w), 2918 (w), 2851 (w), 2068 (s), 2022 (s), 2011 (s), 1977 (vs), 1932 (s), 1429 (m), 1371 (m), 1220 (m),1038 (m), 834 (m) cm^{-1}.

[2,3,4,5-Tetra(5-methylthien-2-yl)cyclopentadienone]iron tricarbonyl (3c): 1,2-bis(5-methylthien-2-yl)ethynylene **1c** (500 mg, 2.29 mmol), Fe(CO)$_5$ (3.16 mL, 11.5 mmol), toluene (30 mL); 110 °C for 15 d; LC: SiO$_2$, PE; CPD-FeCO$_3$ complex **3c** (609 mg, 1.01 mmol, 88%) was isolated as yellow solid. Mp >90 °C (decomp.); ^{1}H-NMR (400 MHz, THF-d$_8$) δ=6.65 (d, ^3J=3.6 Hz, 2 H, *H-3*), 6.49 (d, ^3J=3.6 Hz, 2 H, *H-3*), 6.46 (td, ^3J=3.6 Hz, ^4J=1.2 Hz, 4 H, *H-4*), 2.31 (d, ^4J=1.2 Hz, 12 H, *CH₃*) ppm; ^{13}C-NMR (101 MHz, THF-d$_8$) δ=214.4, 204.5, 163.2, 150.4, 143.3, 140.7, 134.7, 132.4, 129.8, 127.0, 125.9, 125.9, 15.1, 15.1 ppm; IR $\tilde{v}$ = 3064 (w), 2920 (m), 2855 (w), 2069 (s), 2024 (vs), 1983 (vs), 1932 (vs), 1474 (m), 1440 (m), 1221 (m), 1046 (m), 797 (s) cm^{-1}.

[2,3,4,5-Tetra(5'-methyl-5,2'-bithien-2-yl)cyclopentadienone]iron tricarbonyl (3d): 1,2-bis-(5'-methyl-5,2'-bithien-2-yl)ethynylene **1d** (216 mg, 0.56 mmol), Fe(CO)$_5$ (0.38 mL, 2.82 mmol), toluene (15 mL); 110 °C for 6 d; LC: SiO$_2$, PE/EA 98:2; CPD-FeCO$_3$ complex **3d** (100 mg, 0.11 mmol, 38%) was isolated as red solid. Mp >60 °C (decomp.); ^{1}H-NMR (400 MHz, THF-d$_8$) δ= 6.90-6.86 (m, 10 H, *Th*), 6.69 (d, ^3J=3.7 Hz, 2 H, *Th*), 6.60 (qd, ^3J=3.7 Hz, ^4J=1.4 Hz, 4 H, *H-4*), 2.40 (s, 6 H, *CH₃*), 2.38 (s, 6 H, *CH₃*) ppm; ^{13}C-NMR (101 MHz, THF-d$_8$) δ=213.7, 204.4, 161.9, 150.4, 141.6, 140.8, 140.3, 139.1, 135.4, 135.2, 134.5, 133.6, 128.9, 128.1,

127.1, 127.1, 125.1, 124.6, 123.6, 123.4, 15.3, 15.3 ppm; IR ṽ = 3064 (w), 2914 (w), 2063 (vs), 2024 (vs), 1975 (vs), 1929 (s), 1470 (m), 1440 (m), 1376 (m), 1034 (m), 870 (m), 780 (s) cm^{-1}.

[2,3,4,5-Tetra(5-phenylthien-2-yl)cyclopentadienone]iron tricarbonyl (3e): 1,2-bis(5-phenylthien-2-yl)ethynylene **1e** (130 mg, 0.38 mmol), Fe(CO)$_5$ (0.52 mL, 1.90 mmol), toluene (8 mL); 110 °C for 8 d; LC: SiO$_2$, PE/EA 99:1; CPD-FeCO$_3$ complex **3e** (72 mg, 0.08 mmol, 44%) was isolated as red solid. Mp >60 °C (decomp.); ^{1}H-NMR (400 MHz, THF-d$_8$) δ=7.51 (d, ^3J=7.3 Hz, 4H, *Ph*), 7.47 (d, ^3J=7.3 Hz, 4H, *Ph*) 7.30-7.23 (m, 8H, *Ph, Th*), 7.21-7.16 (m, 8H, *Ph, Th*), 7.01 (d, ^3J=3.8 Hz, 4H, *Th*), 6.80 (d, ^3J=3.8 Hz, 4H, *Th*) ppm; ^{13}C-NMR (101 MHz, THF-d$_8$) δ= 213.8, 204.4, 162.4, 151.7, 147.8, 145.3, 135.9, 134.9, 134.7, 133.8, 129.8, 129.8, 129.3, 128.8, 128.5, 128.4, 126.5, 126.3, 124.0, 123.9 ppm; IR ṽ = 3061 (w), 3023 (w), 2919 (w), 2853 (w), 2066 (vs), 2025 (vs), 1978 (vs), 1926 (s), 1738 (m), 1598 (m), 1442 (m), 952 (m), 797 (m) cm^{-1}.

[2,3,4,5-Tetra(5-formylthien-2-yl)cyclopentadienone]iron tricarbonyl (3f): 1,2-bis(5-formylthien-2-yl)ethynylene **1f** (100 mg, 0.41 mmol), Fe(CO)$_5$ (0.27 mL, 2.03 mmol), toluene (10 mL); 110 °C for 7 d; LC: SiO$_2$, PE/EA = 2:1; CPD-FeCO$_3$ complex **3f** (44 mg, 0.07 mmol, 33%) was isolated as orange solid. Mp >60 °C (decomp.); ^{1}H-NMR (400 MHz, THF-d$_8$) δ=9.72 (s, 2H, *CHO*), 9.71 (s, 2H, *CHO*), 7.63 (d, ^3J=3.9 Hz, 2H, *Th*), 7.58 (d, ^3J=3.9 Hz, 2H, *Th*), 7.16 (d, ^3J=3.9 Hz, 2H, *Th*), 6.98 (d, ^3J=3.9 Hz, 2H, *Th*) ppm; ^{13}C-NMR (101 MHz, THF-d$_8$) δ=211.9, 203.9, 183.3, 183.0, 160.9, 159.7, 147.1, 144.8, 143.7, 137.3, 136.4, 134.1, 129.0, 128.0 ppm; IR ṽ = 3088 (w), 2808 (w), 2738 (w), 2075 (s), 2039 (vs), 1991 (vs), 1652 (vs), 1520 (m), 1205 (s), 1096 (m), 1042 (m), 892 (m), 803 (m), 758 (m) cm^{-1}.

[2,3,4,5-Tetra(*p*-cyanophenyl)cyclopentadienone]iron tricarbonyl (3g): 1,2-bis(*p*-cyanophenyl)ethynylene **1g** (400 mg, 1.75 mmol), Fe(CO)$_5$ (1.18 mL, 8.76 mmol), toluene (30 mL); 130 °C for 7 d; LC: SiO$_2$, PE/EA 4:1; CPD-FeCO$_3$ complex **3g** (301 mg, 0.48 mmol, 55%) was isolated as orange solid. Mp >140 °C (decomp.); ^{1}H-NMR (400 MHz, THF-d$_8$) δ=7.54 (d, ^3J=8.0 Hz, 4H, *Ph*), 7.46 (d, ^3J=8.1 Hz, 4H, *Ph*), 7.27 (d, ^3J=8.1 Hz, 4H, *Ph*), 7.18 (d, ^3J=8.0 Hz, 4H, *Ph*) ppm; ^{13}C-NMR (101 MHz, THF-d$_8$) δ=214.1, 204.5, 171.2, 152.7, 139.3, 135.2, 133.2, 132.7, 129.4, 118.8, 118.5, 113.7, 111.9 ppm; IR ṽ = 2924 (w), 2854 (w), 2229 (s), 2074 (vs), 2036 (vs), 1992 (vs), 1600 (s), 1498 (m), 1462 (m), 1115 (m), 1016 (m), 842 (s) cm^{-1}.

[2,3,4,5-Tetra(*p*-methoxyphenyl)cyclopentadienone]iron tricarbonyl (3h): 1,2-bis(*p*-methoxyphenyl)ethynylene **1h** (300 mg, 1.26 mmol), Fe(CO)$_5$ (0.85 mL, 6.30 mmol), toluene (15 mL); 130 °C for 7 d; LC: SiO$_2$, PE/EA 2:1; CPD-FeCO$_3$ complex **3h** (189 mg, 0.29 mmol, 47%) was isolated as orange solid. Mp >180 °C (decomp.); ^{1}H-NMR (400 MHz, THF-d$_8$) δ=7.64 (d, ^3J=8.9 Hz, 4H, *Ph*), 7.20 (d, ^3J=8.9 Hz, 4H, *Ph*), 6.75-6.72 (m, 8H, *Ph*), 3.73 (s, 6H, *OCH$_3$*), 3.71 (s, 6H, *OCH$_3$*) ppm; ^{13}C-NMR (101 MHz, THF-d$_8$) δ=210.9, 171.5, 160.9, 160.2, 134.4, 132.3, 125.0, 123.6, 114.2, 114.1, 104.4, 82.8, 55.5, 55.4 ppm; HR-MS (ESI+): calcd. for C$_{36}$H$_{28}$FeO$_8$: m/z=645.12070 [M+H]$^+$, found: m/z=645.12100 [M+H]$^+$, $δm/m$= 0.47 ppm; Elemental analysis: calc. (%) for C$_{36}$H$_{28}$FeO$_8$: C 67.09, H 4.38; found: C 67.38, H 4.57; IR ṽ = 2932 (w), 2837 (w), 2360 (w), 2062 (vs), 2022 (s), 1994 (vs), 1620 (s), 1606 (s), 1576 (m), 1458 (s), 1426 (m), 1401 (m), 1400 (m), 1387 (m), 1176 (s), 1125 (m), 1028 (s), 821 (m), 769 (m). The analytical data was in accordance with literature.[25]

[2,3,4,5-Tetra(*p*-formylphenyl)cyclopentadienone)iron tricarbonyl (3i): 1,2-bis(*p*-formylphenyl)ethynylene **1i** (300 mg, 1.28 mmol), Fe(CO)$_5$ (0.87 mL, 6.40 mmol), toluene (15 mL); 110 °C for 3 d; LC: SiO$_2$, PE/EA = 2:1); CPD-FeCO$_3$ complex **3i** (112 mg, 0.18 mmol, 27%) was isolated as orange solid. Mp >100 °C (decomp.); ^{1}H-NMR (400 MHz, THF-d$_8$) δ=9.93 (s, 2H, *CHO*), 9.90 (s, 2H, *CHO*), 7.91 (d, ^3J=8.4 Hz, 4H, *Ph*), 7.76-7.73 (m, 8H, Ph), 7.61 (d, ^3J=8.3 Hz, 4H, *Ph*) ppm; ^{13}C-NMR (101 MHz, THF-d$_8$) δ=209.1, 191.7, 191.5, 170.9, 138.8, 138.1, 137.1, 137.0, 133.7, 131.2, 130.1, 129.9, 105.3, 80.0 ppm; IR ṽ = 2833 (w), 2736 (w), 2357 (w), 2073 (vs), 2010 (vs), 1697 (vs), 1644 (s), 1602 (s), 1382 (m), 1300 (m), 1210 (m), 1170 (m), 1114 (m), 1009 (w), 844 (m), 800 (m), 751 (m) cm^{-1}.

[2,3,4,5-Tetra(5-pyrimidinyl)cyclopentadienone]iron tricarbonyl (3j): 1,2-bis(5-pyrimidinyl)-ethynylene **1j** (200 mg, 1.10 mmol), Fe(CO)$_5$ (0.74 mL, 5.49 mmol), toluene (10 mL); 130 °C for 7 d; LC: SiO$_2$, EA; CPD-FeCO$_3$ complex **3j** (240 mg, 0.45 mmol, 82%) was isolated as orange solid. Mp >160 °C (decomp.); ^{1}H-NMR (400 MHz, THF-d$_8$) δ=8.91 (s, 2H, *H-2*), 8.90 (s, 2H, *H-2*), 8.63 (s, 4H, *H-4*), 8.51 (s, 4H, *H-4*) ppm; ^{13}C-NMR (101 MHz, THF-d$_8$) δ=212.5, 204.5, 163.6, 159.6, 159.4, 158.1, 155.5, 141.5, 130.7, 128.4 ppm; IR ṽ = 3100 (w), 2076 (s), 2038 (vs), 2020 (s), 1985 (vs), 1949 (vs), 1546 (s), 1436 (s), 1415 (m), 1383 (m), 1344 (m), 1192 (m), 781 (m) cm^{-1}.

Typical procedure for the photocatalytic hydrogen evolution reaction.

All experiments were carried out in a dried Schlenk tube under argon atmosphere. THF, TEA, water, and Et_4NOH were degassed with argon by standard laboratory methods prior to use. The hydrogen gas evolution was quantitatively measured by a gas syringe and gas analysis was carried out by GC (Bruker Scion SQ with Restek ShinCarbon ST Micropacked Column, thermal conductivity detector, external calibration). The light source was a 150 W xenon lamp (LOT-LSE 140/160.25C). The corresponding catalyst (1.18 µmol), CuPS (3.65 µmol), and Et_4NOH (12 µmol) were dissolved in a solvent mixture $THF/TEA/H_2O$ (4:3:1, 10 mL). The reaction solution was irradiated at room temperature until no further hydrogen evolution was measured. All values given are the average values of at least three experiments.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Keywords: cyclopentadienone, iron tricarbonyl complex, photocatalysis, hydrogen evolution, cyclic voltammetry

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