

**Transition metal catalyzed Fe-C coupling reactions in synthesis of
dicarbonyl(2-thienylethynyl)(η^5 -cyclopentadienyl)iron complex.
Spectroscopic, structure and electrochemical study.**

Victor V. Verpekin ^{a, 1}, Ivan S. Ahremchik ^a, Alexander D. Vasiliev ^{b, c}, Galina V. Burmakina ^a,
Alexander A. Kondrasenko ^a, Tatyana S. Nedelina ^a, and Arkadii Z. Kreindlin ^d

^a *Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center "Krasnoyarsk Science Center SB RAS", Akademgorodok, 50-24, Krasnoyarsk 660036, Russia*

^b *Institute of Physics SB RAS, Federal Research Center "Krasnoyarsk Science Center SB RAS", Akademgorodok, 50-38, Krasnoyarsk 660036, Russia*

^c *Siberian Federal University, Svobodny prospekt, 79, Krasnoyarsk 660041, Russia*

^d *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow 119991, Russian Federation*

Abstract

The new σ -alkynyl iron(II) complex $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-(2-C}_4\text{H}_3\text{S)}$ was synthesized with application of several known approaches based on the transition metal (Pd/Cu-, Au-, Cu- and Pd-) catalyzed Fe-C coupling reactions of 2-ethynylthiophene or 2-[(trimethylsilyl)ethynyl]thiophene with cyclopentadienyliron dicarbonyl iodide. The yield of the complex in these reactions was found to strongly depend on the catalyst used. The conditions, catalysts, and reagents that provide the highest yields of the desired 2-thienylethynyl iron complex were determined. The complex was characterized by IR, ¹H and ¹³C NMR spectroscopy. The molecular structure of $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-(2-C}_4\text{H}_3\text{S)}$ established by X-ray diffraction analysis exhibits a three leg piano stool geometry. The redox properties of the new complex were studied.

Keywords: iron, thiophene, σ -alkynyl complexes, Pd-catalysis, Fe-C coupling, electrochemistry

¹ Corresponding Author: yvv@icct.ru, yvv@icct.ru (V.V. Verpekin); 0000-0001-9228-7990.

Introduction

Transition metal complexes featuring σ -alkynyl, polyynyl, and polyynediyl ligands have been widely established as promising building blocks for the design of materials possessing optical nonlinearity, light-emitting ability, and electrical conductivity [1–4]. There is also interest in their application in synthetic chemistry [5, 6] and proton reduction catalysis [7, 8]. Therefore, a variety of synthetic approaches to transition metal acetylides are known [9]. Apparently, the most valuable and reliable methods for their synthesis, are based on the ability of some transition metal complexes to catalyze M-C coupling reactions between a metal halide complex and a terminal alkyne [10–13]. In this work we tested the other known Cu-, Au-, Pd/Cu-, and Pd-catalyzed conditions in reactions of 2-ethynylthiophene and 2-[(trimethylsilyl)ethynyl]thiophene with $\text{Cp}(\text{CO})_2\text{FeI}$ in order to develop a route to dicarbonyl(2-thienylethynyl)(η^5 -cyclopentadienyl)iron complex $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-(2-C}_4\text{H}_3\text{S)}$ (**1**). We also report here on spectroscopic, structural and electrochemical characteristics of the complex obtained.

Results and discussion

Our search of conditions for the catalytic preparation of $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-(2-C}_4\text{H}_3\text{S)}$ (**1**) started with the methodology developed by Bruce [12, 14] for the synthesis of a series of transition metal polyne and polyynediyl complexes, where CuI and diethylamine were successfully exploited as a catalyst and a base, respectively. Unfortunately, the reaction of cyclopentadienyliron dicarbonyl iodide (FpI) with 2-ethynylthiophene under these conditions gave only traces of the target complex **1** (Table 1, entry 1). Therefore, we also tested the gold(I) catalyzed coupling, which was shown to be applicable to the preparation of $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-Ph}$ [15]. The coupling between $\text{H-C}\equiv\text{C-(2-C}_4\text{H}_3\text{S)}$ and FpI under $(\text{PPh}_3)\text{AuCl}$ catalysis took place, however, resulting in only 29% yield of the target complex $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-(2-C}_4\text{H}_3\text{S)}$ (**1**) (Table 1, entry 2).

The organometallic analog of the Sonogashira cross-coupling was successfully applied by the Oshima team for the preparation of series of σ -alkynyliron complexes $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-Ar}$ [11]. Indeed, the reaction of cyclopentadienyliron dicarbonyl iodide with 2-ethynylthiophene under Oshima conditions (2.5 mol% of $\text{PdCl}_2(\text{NMe})_2$, 5 mol% of CuI, a 1:2 mixture of

diisopropylamine/THF, room temperature) provided the highest yield (81%) of the complex $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(2-\text{C}_4\text{H}_3\text{S})$ (**1**) (Table 1, entry 3). The nature of the base used in this reaction was found to be important for achieving high yield of **1** under these conditions. For example, the replacement of diisopropylamine by triethylamine or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded at most 34 and 23% of **1** under the otherwise identical conditions. A decrease in the yield of **1** was also observed when the reaction was performed without CuI (Table 1, entry 6).

A moderate (53%) yield of the complex **1** was achieved in the coupling of $\text{Cp}(\text{CO})_2\text{FeI}$ and 2-[(trimethylsilyl)ethynyl]thiophene at 60°C using 10 mol% of $\text{PdCl}_2(\text{NMe})_2$ (Table 1, entry 8). Previously, a synthetic applicability of this approach under Pd/Cu-catalyzed conditions was also demonstrated by the Oshima group [11]. However, the presence of CuI as a cocatalyst in our case did not affect the yield of the product. Thus, this reaction can be considered as an organometallic analog of the Hiyama coupling, where the anionic pentacoordinated silicon moiety should participate in the transfer of 2-thienylacetylide, instead of Cu-acetylide [16].

It should be noted that the Pd/Cu- and Pd-catalyzed coupling reactions of 2-ethynylthiophene and 2-[(trimethylsilyl)ethynyl]thiophene with $\text{Cp}(\text{CO})_2\text{FeI}$ gave **1** along with the dimerization product $[\text{Cp}(\text{CO})_2\text{Fe}]_2$ (Fp_2), the amount of which was relatively high in Pd-catalyzed conditions, but decreased under Pd/Cu-catalyzed conditions. Moreover, complex **1** proved unstable in the reactions mixtures. For example, the reaction of FpI with $\text{H}-\text{C}\equiv\text{C}-(2-\text{C}_4\text{H}_3\text{S})$ in the diisopropylamine/THF mixture for 12 hours afforded **1** in unexpectedly low yield (12%) (Table 1, entry 6), despite its formation in the beginning of the reaction as indicated by IR spectroscopy and TLC. At the same time, in the reaction between FpI and $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-(2-\text{C}_4\text{H}_3\text{S})$ no traces of the complex were detected in the reaction mixture after 12 hours (Table 1, entry 10). The formation and following decomposition of **1** upon prolonged reaction time is also indicated by a consumption of $\text{Cp}(\text{CO})_2\text{FeI}$ which remains almost the same as in the analogous reactions, performed for shorter time (entries 3 and 6, Table 1)

Table 1 Conditions for the synthesis of Cp(CO)₂Fe-C≡C-(2-C₄H₃S) (**1**)^{a)}

#	Alkyne	Catalyst	Base/Solvent	Temp.	Time	Conv. ^{b)} , %	Yield, %	
							1	Fp ₂
1	X = H (1.5 equiv)	CuI 10 mol%	Et ₂ NH (4 mL); CHCl ₃ (8 mL)	60°C	2 hour	6	4	-
2		(PPh ₃)AuCl (10 mol%)	NEt ₃ (2 equiv); CHCl ₃ (3 mL)	60°C	2 hour	32	29	-
3		PdCl ₂ (NCMe) ₂ 2.5 mol%; CuI 5 mol%	ⁱ Pr ₂ NH (4 mL); THF (8 mL)	24°C	0.5 hour	85	81	2
4			NEt ₃ (3 mL); THF (6 mL)	24°C	0.5 hour	37	34	2
5			DBU (1.5 equiv); THF (10 mL)	24°C	0.5 hour	28	23	4
6			ⁱ Pr ₂ NH (4 mL); THF (8 mL)	24°C	12 hours	88	12	7
7		PdCl ₂ (NCMe) ₂ 10 mol%	ⁱ Pr ₂ NH (3 mL); THF (6 mL)	24°C	1 hour	29	14	13
8	X = Si(Me) ₃ (1.5 equiv)	PdCl ₂ (NCMe) ₂ 10 mol%	TBAF (1.5 equiv); THF (10 mL)	60°C	1 hour	78	53	23
9		PdCl ₂ (NCMe) ₂ 10 mol%; CuI 20 mol%	TBAF (1.5 equiv); THF (10 mL)	60°C	1 hour	78	54	21
10		PdCl ₂ (NCMe) ₂ 10 mol%	TBAF (1.5 equiv); THF (5 mL)	60°C	12 hours	81	-	12

^{a)} All reactions were carried out using 1 equiv. Cp(CO)₂FeI

^{b)} Conversion was calculated from the amount of unreacted Cp(CO)₂FeI recovered by column chromatography

Complex Cp(CO)₂Fe-C≡C-(2-C₄H₃S) (**1**) was isolated as a brown-yellow, moderately air-stable solid. It was characterized by elemental analysis, IR, ¹H and ¹³C NMR spectroscopy (see Experimental). The IR and NMR spectroscopic data obtained are similar to those found for analogous cyclopentadienyliron dicarbonyl complexes with different σ-alkynyl ligands [11, 17, 18].

The molecular structure of the complex **1** was established by X-ray diffraction study (Fig. 1). The metal center in **1** has a *pseudo*-octahedral geometry, the coordination environment of iron(II) atom is occupied by the η^5 -cyclopentadienyl ring, two terminal CO groups and by the σ -alkynyl ligand. The values of single Fe-C8 and triple C8-C9 bond lengths (1.921 and 1.196 Å, respectively) are in line with those of the previously reported $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-\text{R}$ complexes [19–22]. The main feature of the complex **1** is the disordering of the thiophene ring over two symmetrical positions with a 1:1 occupancy ratio by a 180° rotation of it around C9-C10 bond. Such disorder is frequently observed for complexes bearing thiophene rings and, unfortunately, precludes the determination of the bond distances and angles in this ring. [23–25].

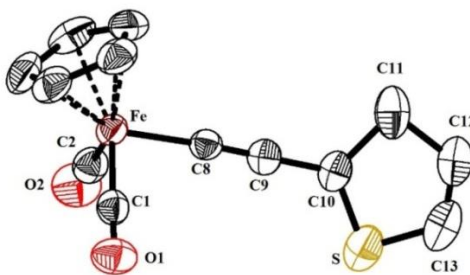


Fig. 1 Molecular structure of $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(2-\text{C}_4\text{H}_3\text{S})$ (**1**). Only one position of the disordered thiophene ring is shown. All hydrogen atoms are omitted for clarity

The redox properties of $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(2-\text{C}_4\text{H}_3\text{S})$ (**1**) were studied in acetonitrile solutions by dc polarography at a dropping mercury electrode (DME) and cyclic voltammetry (CV) at platinum or glassy carbon (GC) electrodes. The electrochemical characteristics² of complex **1**, and, for comparison, of the previously studied *ortho*-pyridylethynyl iron complex $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(2-\text{C}_5\text{H}_4\text{N})$ (**2**) [26] are given in Table 2, their cyclic voltammograms at GC electrode are shown in Fig.1S (the supplementary materials).

² Potentials are given versus Ag/0.1 M AgNO_3 couple in MeCN (they can be converted to V versus SCE by adding 0.337 V).

Table 2 Electrochemical characteristics of the σ -alkynyl iron complexes **1** and **2** (MeCN, 0.1 M [Et₄N]BF₄, 2 mM, Ag/ 0.1 M AgNO₃ in MeCN)

Complex	$E_{1/2}$, V (n)				
	Pt		GC		DME
	Ox	Red	Ox	Red	Red
Cp(CO) ₂ Fe-C≡C-(2-C ₄ H ₃ S) (1)	0.60(1)	-2.09(1)	0.67(1)	-2.16(1) ^{a)}	-2.26(1)
	1.36(1)		1.40(1)		-2.65(1)
Cp(CO) ₂ Fe-C≡C-(2-C ₅ H ₄ N) (2)	0.81 (1)	-2.10 (1)	0.87 (1)	-2.16 (1) ^{a)}	-2.25 (1)
					-2.60 (1)
					-2.95 (<1)

^{a)} The quasi-reversible wave;

n – the number of electrons transferred in a particular electrochemical study (the sign "<" indicates that the wave height of the compound is less than the height of a one-electron wave)

The comparison of the electrochemical data of **1** and **2** (Table 2) clearly shows that their oxidation potentials depend on the nature of the substituents in the σ -alkynyl ligand in contrast to their reduction potentials. The $E_{1/2}$ values of the oxidation wave of Cp(CO)₂Fe-C≡C-(2-C₄H₃S) (**1**) at Pt and GC electrodes are shifted to the cathode region of the potentials relative to $E_{1/2}$ of the oxidation wave of **2** that is consistent with a π -excessive nature of the 2-thienyl substituent in **1** and a π -deficient nature of the 2-pyridyl substituent in **2**. The $E_{1/2}$ values of the reduction of complexes **1** and **2** almost coincide. Thus, one may suggest that: (i) the highest occupied molecular orbitals (HOMO) participating in oxidation processes are likely to be localized on the σ -alkynyl ligands of both complexes, which differ in the nature of their heterocyclic nuclei; (ii) the lowest unoccupied molecular orbitals (LUMO) participating in the reduction processes are likely to be centered on the [Cp(CO)₂Fe]-fragment for both complexes. Previously, the similar localizations of HOMO and LUMO were found for 1,4-dimethoxybutadienediyl-bridged and butadienediyl-bridged diiron complexes [Cp*(PMe₃)(CO)Fe-C(OCH₃)=CH-CH=C(OCH₃)-Fe(PMe₃)(CO)Cp*] and [Cp*(dppe)Fe-(C≡C)₂-Fe(dppe)Cp*] [27].

Conclusion

In summary, several approaches based on the Cu-, Au-, Pd/Cu-, and Pd-catalyzed Fe-C coupling reactions were tested to synthesize dicarbonyl(2-thienylethynyl)(η^5 -cyclopentadienyl)iron complex (**1**). Although, all methods employed in the present work gave the target compound **1**, the most appropriate one proved the coupling reactions of $\text{Cp}(\text{CO})_2\text{FeI}$ and 2-ethynylthiophene under Pd/Cu-catalyzed conditions. Also, the nature of base appears to be an important factor for achieving high yield of the target compound (**1**), the use of the diisopropylamine provided the highest (81%) yield of **1**. The Pd-catalyzed coupling reaction of cyclopentadienyliron dicarbonyl iodide with 2-[(trimethylsilyl)ethynyl]thiophene gave only moderate yields of $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-(2-C}_4\text{H}_3\text{S)}$ (**1**). The coupling of $\text{Cp}(\text{CO})_2\text{FeI}$ with 2-ethynylthiophene under gold-catalyzed conditions afforded the complex in yield of 34%, while only traces of **1** were obtained under Cu-catalysis.

The structural and spectroscopic data obtained showed that the complex **1** is a typical example of dicarbonyl(σ -alkynyl)(η^5 -cyclopentadienyl)iron complexes. The comparison of the electrochemical data of **1** with those of $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-(2-C}_5\text{H}_4\text{N)}$ showed that the oxidation potential of the complexes depends on the nature of the substituent in the σ -alkynyl ligand and, consequently, this ligand contributes to the frontier orbitals of the complexes.

Experimental

Materials and methods

All operations and manipulations were carried out under an argon atmosphere using the Schlenk technique. Solvents (dichloromethane, petroleum ether, ethyl acetate, hexane, triethylamine) were distilled over appropriate drying agents and stored under argon. THF was dried by refluxing over sodium/benzophenone ketyl and freshly distilled prior to use. Neutral silica gel (Silica 60, 0.2-0.5 mm, Macherey-Nagel) was used for column chromatography. Tetrabutylammonium fluoride solution (1M solution in THF, Aldrich), 1,8-Diazabicyclo[5.4.0]undec-7-ene (Aldrich), and catalyst CuI ("Vekton-M" Ltd.) were used as received. $\text{PdCl}_2(\text{NCMe})_2$, $\text{Cp}(\text{CO})_2\text{FeI}$, $(\text{PPh}_3)\text{AuCl}$, 2-ethynylthiophene and 2-[(trimethylsilyl)ethynyl]thiophene were prepared according to the literature procedures [28–31]. The IR spectra were recorded on a Shimadzu IRTracer-100 spectrometer (Japan).

^1H and ^{13}C NMR spectra were obtained using NMR spectrometer AVANCE III 600 (Bruker, Germany). Chemical shifts are reported in ppm units referenced to solvent resonances. The course of reactions was monitored by TLC on silica gel (Alu foils, Sigma-Aldrich) and IR spectroscopy. The X-ray data for complex **1** were collected on a Smart Photon II diffractometer (Bruker AXS, Germany). Crystal data and X-ray experimental details are given in the supplementary materials (Table 1S). The polarograms and cyclic voltammograms (CV) were recorded on an IPC-Pro M potentiostat (Volta, Saint-Petersburg, Russia). The experimental details of the electrochemical measurements are given in the supplementary materials.

Synthesis

Here only the synthetic procedure providing the highest yield of **1** is given; other methods used are described in the supplementary materials. Cyclopentadienyliron dicarbonyl iodide (302 mg, 0.993 mmol) and 2-ethynylthiophene (160 mg, 1.481 mmol) were dissolved in a freshly distilled THF (8 mL), then diisopropylamine (4 mL), $\text{PdCl}_2(\text{NCMe})_2$ (7 mg, 0.027 mmol), and CuI (9 mg, 0.047 mmol) were added. The resulting mixture was stirred at 24°C for 30 minutes, and then was passed through a pad (0.5 cm) of silica gel by using ethyl acetate as the eluent. The filtrate was concentrated *in vacuo* and chromatographed on silica gel (9×2cm). Three fractions were successively eluted with petroleum ether-dichloromethane (9:1), (4:1), (1:1) mixtures. The first light-red fraction gave 4 mg of the dimer $[\text{Cp}(\text{CO})_2\text{Fe}]_2$ (0.011 mmol, 2%). 45 mg (0.148 mmol) of the starting $\text{Cp}(\text{CO})_2\text{FeI}$ was obtained from the second yellow-brown fraction. The target complex $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-(2-C}_4\text{H}_3\text{S)}$ (**1**) was isolated in 81% yield (228 mg, 0.803 mmol) as a brown-yellow solid after evaporation of the solvent from the third dark-yellow fraction. Brown-yellow crystals of dicarbonyl(2-thienylethynyl)(η^5 -cyclopentadienyl)iron (**1**) suitable for X-ray diffraction study were obtained by fast evaporation of a solution of the complex in a dichloromethane : hexane mixture = 1:2. IR (ν/cm^{-1}): 2100s $\nu(\text{C}\equiv\text{C})$, 2043vs, 1996vs $\nu(\text{CO})$ (CH_2Cl_2); 2094s $\nu(\text{C}\equiv\text{C})$, 2034vs, 1989vs $\nu(\text{CO})$ (KBr). ^1H NMR (CDCl_3 , 25°C) δ , ppm [J , Hz]: 5.06 (s, 5H, C_5H_5); 6.85 (s, 1H, **H4**); 6.92 (br., 1H, **H3**); 6.93 (br., 1H, **H2**). ^{13}C NMR (CDCl_3 , 25°C) δ , ppm [J , Hz]: 85.3 (C_5H_5); 95.2 ($\equiv\text{C}^2$); 107.7 ($\text{C}^1\equiv$); 122.6 ($\text{C}2$ of $\text{C}_4\text{H}_3\text{S}$); 126.1 ($\text{C}3$ of $\text{C}_4\text{H}_3\text{S}$); 128.2 ($\text{C}4$ of $\text{C}_4\text{H}_3\text{S}$); 128.6 (C_{ipso} of $\text{C}_4\text{H}_3\text{S}$); 212.0 (2Fe-CO). Anal. Found: C, 55.1%; H, 2.8%; S, 11.3%. Calc. For $\text{C}_{13}\text{H}_8\text{FeO}_2\text{S}$ (284): C, 55.0%; H, 2.8%; S, 11.3%.

Supplementary material

General Information on used reagents and equipment; General procedure for all performed coupling reactions; Analytical data; Detailed descriptions of X-ray diffraction study; Table 1S: Crystal data and X-ray experimental details of **1** (CCDC 1996445).

Funding

This research was funded by a grant from the Russian Science Foundation (project № 18-73-00150).

Acknowledgments

Physicochemical characteristics were obtained at the Krasnoyarsk Regional Centre of Research Equipment, Siberian Branch of the Russian Academy of Sciences.

Conflicts of interest

The authors declare that they have no conflicts of interest.

Authors' contributions

Victor V. Verpekin: Conceptualization, Funding acquisition, Investigation, Methodology, Supervision, Writing. **Ivan S. Ahremchik**: Investigation. **Alexander D. Vasiliev**: X-ray diffractometry investigation. **Galina V. Burmakina**: Electrochemical investigation. **Alexander A. Kondrasenko**: NMR investigation. **Tatyana S. Nedelina**: Electrochemical investigation. **Arkadii Z. Kreindlin**: investigation.

References

1. Low PJ (2013) Twists and turns: Studies of the complexes and properties of bimetallic complexes featuring phenylene ethynylene and related bridging ligands. *Coord Chem Rev* 257:1507–1532. <https://doi.org/10.1016/j.ccr.2012.08.008>
2. Grelaud G, Cifuentes MP, Paul F, Humphrey MG (2014) Group 8 metal alkynyl complexes for nonlinear optics. *J Organomet Chem* 751:181–200. <https://doi.org/10.1016/j.jorganchem.2013.10.008>
3. Yam VW-W, Au VK-M, Leung SY-L (2015) Light-Emitting Self-Assembled Materials Based on d 8 and d 10 Transition Metal Complexes. *Chem Rev* 115:7589–7728. <https://doi.org/10.1021/acs.chemrev.5b00074>
4. Li Y-P, Fan X-X, Wu Y, et al (2017) High-efficiency organic light-emitting diodes of

- phosphorescent PtAg₂ heterotrinnuclear acetylide complexes supported by triphosphine. *J Mater Chem C* 5:3072–3078. <https://doi.org/10.1039/C7TC00382J>
5. Nakaya R, Yasuda S, Yorimitsu H, Oshima K (2011) (1-Alkynyl)dicarbonylcyclopentadienyliron Complexes as Electron-Rich Alkynes in Organic Synthesis: BF₃-Mediated [2+2] Cycloaddition/Ring-Opening Providing (2-Alkenyl-1-imino)iron Complexes. *Chem - A Eur J* 17:8559–8561. <https://doi.org/10.1002/chem.201100669>
 6. Akita M, Koike T (2008) Chemistry of polycarbon species: from clusters to molecular devices. *Dalt Trans* 9226:3523–3530. <https://doi.org/10.1039/b802069h>
 7. Valyaev DA, Peterleitner MG, Semeikin O V., et al (2007) Proton reduction catalysis by manganese vinylidene and allenylidene complexes. *J Organomet Chem* 692:3207–3211. <https://doi.org/10.1016/j.jorganchem.2007.01.055>
 8. Kaim V, Kaur-Ghumaan S (2019) Manganese Complexes: Hydrogen Generation and Oxidation. *Eur J Inorg Chem* 2019:5041–5051. <https://doi.org/10.1002/ejic.201900988>
 9. Long NJ, Williams CK (2003) Metal alkynyl σ complexes: Synthesis and materials. *Angew Chemie - Int Ed* 42:2586–2617. <https://doi.org/10.1002/anie.200200537>
 10. Lo Sterzo C (1999) The Wonder of Palladium Catalysis: From Carbon-Carbon to Metal-Carbon Bond Formation. An Opportunity of Getting Astonishment from Reality. *Synlett* 1999:1704–1722. <https://doi.org/10.1055/s-1999-2919>
 11. Nakaya R, Yasuda S, Yorimitsu H, Oshima K (2009) Synthesis of (1-alkynyl)dicarbonylcyclopentadienyliron complexes by palladium-catalyzed Sonogashira-type carbon-iron bond formation. *Tetrahedron Lett* 50:5274–5276. <https://doi.org/10.1016/j.tetlet.2009.07.005>
 12. Bruce MI, Ke M, Low PJ (1996) Syntheses of metal diyne complexes: novel routes to all-carbon ligands. *Chem Commun* 3:2405–2406. <https://doi.org/10.1039/cc9960002405>
 13. Osakada K, Yamamoto T (2000) Transmetallation of alkynyl and aryl complexes of Group 10 transition metals. *Coord Chem Rev* 198:379–399. [https://doi.org/10.1016/S0010-8545\(99\)00210-6](https://doi.org/10.1016/S0010-8545(99)00210-6)

14. Bruce MI, Ke M, Low PJ, et al (1998) Syntheses and Chemistry of the Diynyl Complexes $M(C\equiv CC\equiv CH)(CO)_3(\eta-C_5H_5)$ ($M = Mo, W$): Crystal Structures of $W(C\equiv CC\equiv CSiMe_3)(CO)_3(\eta-C_5H_5)$, $W\{C\equiv CC[CH=C(CN)_2]=C(CN)_2\}(CO)_3(\eta-C_5H_5)$, and *cis*- $W(C\equiv CPh)(CO)_2(PPh_3)(\eta-C_5H_5)$. *Organometallics* 17:3539–3549. <https://doi.org/10.1021/om980031r>
15. Hashmi ASK, Molinari L (2011) Effective Transmetalation from Gold to Iron or Ruthenium. *Organometallics* 30:3457–3460. <https://doi.org/10.1021/om200360q>
16. Hiyama T (2002) How I came across the silicon-based cross-coupling reaction. *J Organomet Chem* 653:58–61. [https://doi.org/10.1016/S0022-328X\(02\)01157-9](https://doi.org/10.1016/S0022-328X(02)01157-9)
17. Crescenzi R, Lo Sterzo C (1992) Synthesis of Metal Acetylides via Palladium-Catalyzed Carbon-Metal Bond Formation. *Organometallics* 11:4301–4305. <https://doi.org/10.1021/om00060a056>
18. Pilar Gamasa M, Gimeno J, Lastra E, et al (1991) Synthesis and characterization of novel σ -alkynyl cyclopentadienyl iron(II) complexes $[Fe(C\equiv CR)L_2(\eta-C_5H_5)]$ [$L = CO$; $L_2 =$ bis(diphenylphosphino)methane (dppm)]. Crystal structure of $[Fe(C\equiv CC_6H_5)(dppm)(\eta-C_5H_5)]$. *J Organomet Chem* 405:333–345. [https://doi.org/10.1016/0022-328X\(91\)86292-X](https://doi.org/10.1016/0022-328X(91)86292-X)
19. Akita M, Terada M, Oyama S, Morooka Y (1990) Preparation, structure, and divergent fluxional behavior of cationic dinuclear iron acetylides $[Fp^*_2(C\equiv CR)]BF_4$ ($R = H, Ph$). *Organometallics* 9:816–825. <https://doi.org/10.1021/om00117a043>
20. Goddard R, Howard J, Woodward P (1974) Crystal and molecular structure of 1-(dicarbonyl- π -cyclopentadienylferrio)-2-(phenyl)-ethyne. *J Chem Soc, Dalt Trans* 2025–2027. <https://doi.org/10.1039/DT9740002025>
21. Steiner T, Tamm M (1998) Weak hydrogen bonds from Cp donors to $C\equiv C$ acceptors. *J Organomet Chem* 570:235–239. [https://doi.org/10.1016/S0022-328X\(98\)00867-5](https://doi.org/10.1016/S0022-328X(98)00867-5)
22. Aechter B, Polborn K, Weinrich V, Beck W (1999) *p*-Tolyl(trimethylsilylethynyl)sulfone as Synthon for the Synthesis of $Cp(OC)_2M-C\equiv CSiMe_3$ ($M = Fe, Ru$). Molecular Structure of $Cp(OC)_2Fe-C\equiv CSiMe_3$. *Zeitschrift für Naturforsch B* 54:701–704. <https://doi.org/10.1515/znb-1999-0521>

23. Roué S, Le Stang S, Toupet L, Lapinte C (2003) Magnetic communication between two $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})\text{Fe(III)}]$ units mediated by the 2,5-bis(ethynyl)thiophene spacer. *Comptes Rendus Chim* 6:353–366. [https://doi.org/10.1016/S1631-0748\(03\)00051-1](https://doi.org/10.1016/S1631-0748(03)00051-1)
24. Bock S, Al-Owaedi OA, Eaves SG, et al (2017) Single-Molecule Conductance Studies of Organometallic Complexes Bearing 3-Thienyl Contacting Groups. *Chem - A Eur J* 23:2133–2143. <https://doi.org/10.1002/chem.201604565>
25. Mrózek O, Melounková L, Dostál L, et al (2019) Enhanced cytotoxicity of indenyl molybdenum(ii) compounds bearing a thiophene function. *Dalt Trans* 48:11361–11373. <https://doi.org/10.1039/C9DT01698H>
26. Verpekin V V., Burmakina G V., Zimonin D V., et al (2017) Electrochemical Study of a Heterobinuclear pyridylvinylidene Complex $\text{Cp}(\text{CO})_2\text{Fe} [\mu\text{-C}=\text{CH}(2\text{-C}_5\text{H}_4\text{N})]\text{PdI}$. *J Sib Fed Univ Chem* 10:428–436. <https://doi.org/10.17516/1998-2836-0038>
27. Sahnoune H, Mahias V, Halet J-F, Lapinte C (2019) 1,4-Dimethoxybutadienediyl-Bridged Diiron Compounds in Three Oxidation States: Evaluation of Delocalization Effects. *Organometallics* 38:2724–2737. <https://doi.org/10.1021/acs.organomet.9b00174>
28. Anderson GK, Lin M, Sen A, Gretz E (1990) Bis(Benzonitrile)Dichloro Complexes of Palladium and Platinum. In: Angelici RJ (ed) *Inorganic synthesis*, Vol.28. pp 60–63
29. King RB, Stone FGA, Jolly WL, et al (1963) Cyclopentadienyl Metal Carbonyls and Some Derivatives. In: Jacob Kleinberg (ed) *Inorganic Syntheses*, Volume 7. John Wiley & Sons, Ltd, pp 99–115
30. Braunstein P, Lehner H, Matt D, et al (1990) Platinum-Gold Cluster: Chloro- $1\kappa\text{C}^1$ -Bis(Triethylphosphine- $1\kappa\text{P}$)Bis(Triphenylphosphine)- $2\kappa\text{P}$, $3\kappa\text{P}$ -Triangulo-Digold-Platinum(1+) Trifluoromethanesulfonate. In: Alvin P. Ginsberg (ed) *Inorganic Syntheses*. John Wiley & Sons, Ltd, pp 218–221
31. Weingand V, Wurm T, Vethacke V, et al (2018) Intermolecular Desymmetrizing Gold-Catalyzed Yne-Yne Reaction of Push-Pull Diarylalkynes. *Chem - A Eur J* 24:3725–3728. <https://doi.org/10.1002/chem.201800360>