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Studies on the synthesis, characterization and reactivity of new ferrocenylacetylenylbiphenyl derivatives

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Abstract

A series of ferrocenylacetylenylbiphenyl derivatives Fc-C=C-R [R = C₆H₄-C₆H₅ (1), C₆H₄-C₆H₄-I (2), C₆H₄-C₆H₄-NO₂ (3), C₆H₃(NO₂)-C₆H₄I (4)] and Fc-C=C-R'-C=C-R'' [R'' = Fc, R' = C₆H₄-C₆H₄ (5), C₆H₃(NO₂)-C₆H₄ (6); R'' = C₆H₅, R' = C₆H₄-C₆H₄ (7)] were synthesized from FcC=CH and biphenyl iodides by the Castro–Stephens and Sonogashira coupling reactions, in which compounds 1, 2, 3, 4, 6 and 7 are new. Seven new complexes [Fc-C=C-R][Co₂(CO)₆] [R = C₆H₄-C₆H₅ (8), C₆H₄-C₆H₄-I (9), C₆H₄-C₆H₄-NO₂ (10), C₆H₃(NO₂)-C₆H₄I (11)] and [Fc-C=C-R'-C=C-R''] [Co₂(CO)₆]₂ [R'' = Fc, R' = C₆H₄-C₆H₄ (12), C₆H₃(NO₂)-C₆H₄ (13); R'' = C₆H₅, R' = C₆H₄-C₆H₄ (14)] were obtained by the reaction of the ligands Fc-C=C-R and Fc-C=C-R'-C=C-R'' with Co₂(CO)₈, respectively. Compounds 1-7 and their complexes 8-14 have been characterized by element analysis and spectroscopy, as well as by X-ray diffraction for 1, 4, 8, 9 and 11. The electrochemical data of compounds 1-12 have been obtained by cyclic voltammetry.

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Keywords: Ethynylferrocene; Coupling reaction; Biphenyl derivative; Cobalt carbonyl complex

1. Introduction

In recent years, the design of materials for application in molecular wires has focused on how to arrange organometallic redox-active centers to enhance the capability of transferring electrons along a conjugated molecular axis [1–3]. The diyne $\text{Co}_2(\text{CO})_6$ complexes are probably better candidates and have displayed some electronic communication and interactions between redox-active centers [4–6]. A variety of ferrocenyl π -conjugated derivatives have been designed and synthesized by Castro–Stephens, Sonogashira and other coupling reactions [7–13] because these compounds can be used as an approach to construct linear donor- π -conjugated spacer-accepter assemblies. π -Conjugated compounds with aryl groups have largely been reported [14–16], but ferrocenylacetylenylbiphenyl derivatives are rare [17]. Here we describe the preparation and structural characterization of seven ferrocenylacetylenylbiphenyl derivatives Fc-C=C-R $[R = C_6H_4-C_6H_5]$ (1), $C_6H_4-C_6H_4-I$ (2), $C_6H_4-C_6H_4-NO_2$ (3), $C_6H_3(NO_2) C_6H_4I$ (4)] and $Fc-C \equiv C-R'-C \equiv C-R''$ [R'' = Fc, $R' = C_6H_4 - C_6H_4$ (5), $C_6H_3(NO_2) - C_6H_4$ (6); $R'' = C_6H_5$, $R' = C_6H_4 - C_6H_4$ (7)], in which 1, 2, 3, 4, 6 and 7 are new compounds. Compound 1 was synthesized by the Castro-Stephens coupling reaction of Fc-C=C-Cu and $I-C_6H_4-C_6H_5$, and compounds 2-4 were obtained by the Sonogashira coupling reaction of ethynylferrocene with the relevant iodobiphenyl derivatives, and compounds 5-7 were prepared by a second Sonogashira coupling reaction of ethynylferrocene with compounds 2 and 4, or ethynylbenzene with compound 2, respectively. Seven new cobalt carbonyl complexes [Fc-C \equiv C-R $[Co_2(CO)_6]$ [R = C₆H₄ $-C_6H_5$ (8), $C_6H_4-C_6H_4-I$ (9), $C_6H_4-C_6H_4-NO_2$ (10),

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C₆H₃(NO₂)–C₆H₄I (11)] and [Fc-C=C–R'–C=C–R"]-[Co₂(CO)₆]₂ [R" = Fc, R' = C₆H₄–C₆H₄ (12), C₆H₃(NO₂) –C₆H₄ (13); R" = C₆H₅, R' = C₆H₄–C₆H₄ (14)] have successfully been synthesized by using the reactivity of the alkyne bonds of compounds 1–7 with Co₂(CO)₈. The molecular and crystal structures of compounds 1, 4 and complexes 8, 9 and 11 have been determined by X-ray single crystal analysis. The electrochemical properties of compounds 5, 6 and 12 reveal that no significant electronic communication between the two ferrocenyl units was observed.

2. Experimental

Published procedures or extensions thereof were used to synthesize the initial intermediates Fc-C \equiv CH, Fc-C \equiv CCu [8], C₆H₅C₆H₄I, IC₆H₄-C₆H₄I, IC₆H₄-C₆H₄NO₂, IC₆H₃(NO₂)-C₆H₄I [18,19]. Other chemicals were purchased and used as received.

Unless stated otherwise, all reactions and manipulations were carried out using standard Schlenk techniques under an atmosphere of inert gases. Solvents were purified, dried and distilled under a nitrogen atmosphere prior to use. Reactions were monitored by TLC. Chromatographic separations and purifications were performed on 200–300 mesh silica gel or neutral alumina.

IR spectra were recorded on a Nicolet FTIR spectrometer as KBr discs. Elemental analyses were carried out on an Elementar var III-type analyzer. ¹H and ¹³C NMR spectra in CDCl₃ were recorded on an Inova 500FT-MHz spectrometer. The mass spectra were determined using a Polaris Q MS and a Micromass Autospec ultima- TOF instrument. The electrochemical properties were determined with a BAS 100A-type analyzer. Melting points were recorded using XT-4 melting point apparatus.

2.1. Synthesis of 4-ferrocenylacetylenylbiphenyl (1)

Fc-C \equiv CCu (304 mg, 1.12 mmol) and C₆H₅C₆H₄I (313 mg, 1.12 mmol) were dissolved in 15 ml pyridine. The mixture solution was stirred for 8 h under reflux. The solvent of the resulting brown mixture was removed in vacuum. The residue was dissolved in a minimal amount of CH₂Cl₂. The filtrate was concentrated and subjected to chromatographic separation on a neutral alumina column $(2 \times 30 \text{ cm})$. Elution with hexane–benzene (10:1, v/v) afforded an orange band 1. The yellow solid 1 was obtained by crystallizing from hexane-benzene. Yield, 46%. m.p. 149-151 °C. Anal. Calc. for C₂₄H₁₈Fe: C, 79.58; H, 5.01. Found: C, 78.92; H, 4.98%. IR (KBr disk): $v(C \equiv C)$ 2218 (m) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.26–7.62 (m, 9H, $C_6H_4-C_6H_5$, 4.28 (s, 5H, C_5H_5), 4.54 (s, 4H, C_5H_4). ¹³C NMR (DCCl₃, δ): 122.88, 126.95, 127.50, 128.83, 131.78, 140.33, 140.47 (C_6H_4 - C_6H_5), 85.63, 89.08 (C=C), 65.41, 68.93, 70.07, 71.47 (Cp). MS (EI, m/z, relative abundance): 362 (M⁺, 100%).

2.2. Syntheses of ferrocenylacetylenylbiphenyl derivatives 2 and 5

Ethynylferrocene (375 mg, 1.79 mmol) and 4,4'- diiodobiphenyl (501 mg, 1.79 mmol) were stirred in diisopropylamine (20 ml) with Pd(PPh₃)₂Cl₂ (30 mg, 0.04 mmol) and Cu(OAc)₂ (4 mg, 0.02 mmol) for 20 h under reflux. The solvent of the resulting orange mixture was removed in vacuum. The residue was dissolved in a minimal amount of CH₂Cl₂. The filtrate was concentrated and subjected to chromatographic separation on a neutral alumina column $(2 \times 30 \text{ cm})$. Elution with hexane-dichloromethane (4:1) for 2; 2:1 for 5, v/v) afforded a yellow band 2 and an orange band 5. Yellow crystalline 2 was obtained by re-crystallizing from hexane–dichloromethane at -20 °C. Yield, 11%. m.p. 191 °C. Anal. Calc. for C24H17FeI: C, 59.05; H, 3.51. Found: C, 59.43; H, 3.54%. IR (KBr disk): v(C=C) 2197 (m) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.16–7.79 (m, 8H, $C_6H_4-C_6H_4$), 4.63 (s, 5H, C_5H_5), 4.95 (br s, 4H, C_5H_4). ¹³C NMR (DCCl₃, δ): 93.28, 123.39, 126.67, 128.76, 131.89, 137.92, 139.09, 139.96 (C₆H₄-C₆H₄), 85.47, 89.51 (C≡C), 65.33, 69.05, 70.13, 71.53 (Cp). MS (EI, m/z, relative abundance): 488 (M^+ , 13%). Orange crystalline 5 was obtained by re-crystallizing from THF at room temperature. Yield, 34%. m.p. 233 °C (dec.). Anal. Calc. for C₃₆H₂₆Fe₂: C, 75.82; H, 4.60. Found: C, 75.07; H, 4.49%. IR (KBr disk): $v(C \equiv C)$ 2208 (m) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.48–7.70 (m, 8H, C₆H₄–C₆H₄), 4.42 (br s, 14H, C₅H₅, C₅H₄), 4.70 (br s, 4H, C₅H₄). ¹³C NMR (DCCl₃, δ): 123.14, 126.73, 131.83, 139.51 (C_6H_4 – C_6H_4), 85.59, 89.38 (C \equiv C), 68.99, 70.10, 71.50 (Cp). MS (EI, *m/z*, relative abundance): 570 (M⁺, 9%).

2.3. Syntheses of new compounds 3, 4, 6 and 7

For the syntheses of the new compounds 3, 4, 6 and 7 see Table 1, the separation method being similar to that of compounds 1, 2 and 5. The chemical and spectroscopic characterization are as follows:

Compound **3**: *Anal.* Calc. for $C_{24}H_{17}FeNO_2$: C, 70.78; H, 4.21; N, 3.44. Found: C, 70.62; H, 4.14; N, 3.46%. IR (KBr disk): $v(C \equiv C)$ 2203 (m), $v_{asNO_2}1507$ (s), v_{sNO_2} 1341 (vs) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.26–8.32 (m, 8H, C_6H_4 – C_6H_4), 4.40 (s, 5H, C_5H_5), 4.68 (br s, 4H, C_5H_4). ¹³C NMR (DCCl₃, δ): 124.18, 124.81, 127.22, 127.58, 132.05, 137.61, 146.82, 147.13 (C_6H_4 – C_6H_4), 85.20, 90.62 ($C \equiv C$), 65.01, 69.20, 70.17, 71.61 (Cp). MS (EI, *m/z*, relative abundance): 407 (M⁺, 100%).

Compound 4: Anal. Calc. for $C_{24}H_{16}FeINO_2$: C, 54.03; H, 3.19; N, 2.63. Found: C, 53.93; H, 3.00; N, 2.66%. IR (KBr disk): $\nu(C \equiv C)$ 2208 (m), $\nu_{asNO_2}1527$ (vs), $\nu_{sNO_2}1358$ (s) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.04–7.92 (m, 7H, $C_6H_3 - C_6H_4$), 4.33 (s, 5H, C_5H_5), 4.60 (br s, 4H, C_5H_4). ¹³C NMR (DCCl₃, δ): 94.48, 125.04, 126.71, 129.59, 131.63, 133.86, 134.70, 136.54, 137.88, 148.84 ($C_6H_3 - C_6H_4$), 83.24, 92.54 ($C \equiv C$), 63.93, 69.53, 70.25,

Table 1					
Syntheses of new	compounds 3 ,	4,	6	and	7

Reactants ^a	Catalyst ^b	Time (h)	Product	Yield (%)	m.p. (°C)
Ethynylferrocene and 4-nitro-4'-iodo-biphenyl	А	20	3	51	216-217
Ethynylferrocene and 2-nitro-4,4'-diiodo-biphenyl	А	19	4	31	157-158
			6	15	179–180
Ethynylbenzene and 4-iodo-4'-ferrocenylethynyl-biphenyl	В	16	7	69	240 (dec.)

^a Mol ratio = 1:1 (for 3, 4, 6), 1:2 (for 7); solvent: diethylamine (for 3, 4, 6), THF/diisopropylamine (V:V = 3:1, for 7); reaction temperature: reflux (for 3, 4, 6), 60 °C (for 7).

^b A: Pd(PPh₃)₂Cl₂/CuI (1:1, 2.4 mol%), B: Pd(PPh₃)₂Cl₂/Cu(OAc)₂ (1:1, 6 mol%).

71.78 (Cp). MS (EI, m/z, relative abundance): 533 (M⁺, 16%).

Compound **6**: Anal. Calc. for $C_{36}H_{25}Fe_2NO_2$: C, 70.24; H, 4.06, N, 2.28. Found: C, 69.66; H, 4.11, N, 2.39%. IR (KBr disk): $v(C \equiv C)$ 2208 (m), $v_{asNO_2}1537$ (vs), $v_{sNO_2}1358$ (s) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.23–7.58 (m, 7H, C₆H₃–C₆H₄), 4.24 (s, 14H, C₅H₅, C₅H₄), 4.50 (s, 4H, C₅H₄). ¹³C NMR (DCCl₃, δ): 122.44, 123.25, 123.31, 126.81, 128.31, 128.37, 131.62, 131.86, 132.09, 139.39, 140.16 (C₆H₃–C₆H₄), 85.56, 89.25, 89.48, 92.30 (C = C), 65.19, 68.90, 69.99, 71.45 (Cp). MS (EI, *m/z*, relative abundance): 615 (M⁺, 43%).

Compound 7: *Anal.* Calc. for $C_{32}H_{22}Fe: C, 83.12; H, 4.76. Found: C, 83.70; H, 4.89%. IR (KBr disk): <math>v(C \equiv C)$ 2203 (m) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.26–7.96 (m, 13H, C₆H₄–C₆H₄, C₆H₅), 4.29 (br s, 5H, C₅H₅), 4.54 (br s, 4H, C₅H₄). ¹³C NMR (DCCl₃, δ): 124.30, 124.77, 126.69, 127.80, 131.69, 134.41, 134.60, 136.04, 149.02 (C₆H₄–C₆H₄, C₆H₅), 83.36, 85.26, 89.97, 92.34 (C = C), 64.95, 69.35, 70.09, 71.66 (Cp). MS (EI, *m/z*, relative abundance): 462 (M⁺, 100%).

2.4. Synthesis of complex $[Fc-C \equiv C - C_6H_4 - C_6H_5][Co_2(CO)_6]$ (8)

A benzene solution of equimolar amounts of compounds $Fc-C \equiv C - C_6H_4 - C_6H_5$ (1) and $Co_2(CO)_8$ was stirred for 4 h at 20 °C. The solvent of the resulting black mixture was removed in vacuum. The residue was dissolved in a minimal amount of benzene and subjected to chromatographic separation on a silica gel column (1.2 × 30 cm). Elution with hexane-benzene (10:1) afforded a black band. Crystals of the complex [Fc- $C \equiv C - C_6H_4 - C_6H_5$][Co₂(CO)₆] (8) were obtained by recrystallizing the black solid from hexane-dichloromethane

Table 2 Syntheses of new complexes **9**, **10**, **11**, **12**, **13** and **14**

at -20 °C. Complex 8: Yield, 61%. m.p. 119-120 °C. Anal. Calc. for C₃₀H₁₈Co₂FeO₆: C, 55.59; H, 2.80. Found: C, 55.83; H, 3.19%. IR (KBr disk) v(CO) 2085 (s), 2049 (vs), 2008 (vs) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.26–7.96 (m, 9H, $C_6H_4-C_6H_5$, 4.21 (s, 5H, C_5H_5), 4.44, 4.54 (2s, 4H, C_5H_4). ¹³C NMR (DCCl₃, δ): 199.45 (CO), 92.36, 126.96, 128.90. 127.46. 127.57. 137.66. 140.46. 140.85 $(C_6H_4 - C_6H_5)$, 85.26, 91.16 (C=C), 69.36, 69.66, 70.10 (Cp). MS (FAB, relative abundance): 648 (M⁺, 4%), 592 $(M^+-2CO, 41\%)$, 564 $(M^+-3CO, 100\%)$, 508 $(M^+-5CO, 100\%)$ 53%), 480 (M⁺-6CO, 58%).

2.5. Syntheses of new complexes 9, 10, 11, 12, 13 and 14

The syntheses of new complexes 9, 10, 11, 12, 13 and 14, see Table 2, and the separation method is similar to that of complex 8. The chemical and spectroscopic characterizations are as follows:

Complex 9: Anal. Calc. for $C_{30}H_{17}Co_2FeIO_6$: C, 46.55; H, 2.31. Found: C, 46.52; H, 2.37%. IR (KBr disk) ν (CO) 2080 (s), 2044 (vs), 2008 (vs) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.17–7.88 (m, 8H, C₆H₄—C₆H₄), 4.12 (br s, 5H, C₅H₅), 4.37 (br s, 4H, C₅H₄). ¹³C NMR (DCCl₃, δ): 199.38 (CO), 127.25, 130.24 (C₆H₄—C₆H₄), 85.20 (C=C), 69.38, 69.66, 70.12 (Cp). MS (FAB, relative abundance): 718 (M⁺-2CO, 9%), 690 (M⁺-3CO, 58%), 662 (M⁺-4CO, 24%), 634 (M⁺-5CO, 14%), 606 (M⁺-6CO, 18%).

Complex **10**: Anal. Calc. for $C_{30}H_{17}Co_2FeNO_8$: C, 51.96; H, 2.47; N, 2.02. Found: C, 52.06; H, 2.65; N, 2.16%. IR (KBr disk) v(CO) 2077 (s), 2044 (vs), 2011 (vs) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.24–8.33 (m, 8H, C₆H₄–C₆H₄), 4.19 (s, 5H, C₅H₅), 4.44, 4.50 (d, 4H, C₅H₄). ¹³C NMR (DCCl₃, δ): 199.23 (CO), 124.28, 127.58, 127.82, 130.34, 137.92, 139.98, 146.83 (C₆H₄–C₆H₄), 85.02, 90.08 (C=C), 69.50, 69.68, 70.12

Reactants ^a	Temperature (°C)	Time (h)	Product	Yield (%)	m.p. (°C)
Fc-C \equiv C $-$ C ₆ H ₄ $-$ C ₆ H ₄ $-$ I and Co ₂ (CO) ₈	35	4	9	65	150 (dec.)
$Fc-C \equiv C - C_6H_4 - C_6H_4 - NO_2$ and $Co_2(CO)_8$	50	0.5	10	73	131 (dec.)
Fc-C \equiv C $-$ C ₆ H ₃ (NO ₂) $-$ C ₆ H ₄ I and Co ₂ (CO) ₈	20	0.5	11	90	121 (dec.)
$Fc-C \equiv C - C_6H_4 - C_6H_4 - C \equiv C-Fc$ and $Co_2(CO)_8$	60	1	12	93	110 (dec.)
$Fc-C \equiv C - C_6H_3(NO_2) - C_6H_4 - C \equiv C-Fc \text{ and } Co_2(CO)_8$	40	1	13	74	134 (dec.)
$Fc-C = C - C_6H_4 - C_6H_4 - C = C - C_6H_5 \text{ and } Co_2(CO)_8$	40	1	14	68	168 (dec.)

^a Mol ratio = 1:1 (for 9, 10, 11), 1:2 (for 12, 13, 14); solvent: benzene.

(Cp). MS (FAB, relative abundance): 609 (M^+ -3CO, 32%), 581 (M^+ -4CO, 21%), 553 (M^+ -5CO, 6%), 525 (M^+ -6CO, 7%).

Complex 11: Anal. Calc. for $C_{30}H_{16}Co_2FeINO_8$: C, 43.96; H, 1.95; N, 1.71. Found: C, 43.29; H, 2.18; N, 1.67%. IR (KBr disk) v(CO) 2090 (s), 2049 (vs), 2013 (vs) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.12–8.46 (m, 7H, $C_6H_3-C_6H_4$), 4.22 (br s, 5H, C_5H_5), 4.47 (br s, 4H, C_5H_4). ¹³C NMR (DCCl₃, δ): 198.78 (CO), 92.31, 94.58, 123.79, 129.60, 132.57, 133.98, 136.62, 137.96, 140.72, 148.98 ($C_6H_3-C_6H_4$), 84.16, 86.52 (C=C), 69.79, 69.97, 71.67 (Cp). MS (FAB, relative abundance): 763 (M⁺-2CO, 16%), 735 (M⁺-3CO, 100%), 707 (M⁺-4CO, 62%), 651 (M⁺-6CO, 47%).

Complex **12**: *Anal.* Calc. for $C_{48}H_{26}Co_4Fe_2O_{12}$: C, 50.48; H, 2.29%. Found: C, 50.96; H, 3.20%. IR (KBr disk), ν (CO): 2085 (s), 2049 (vs), 2013 (vs) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.26–7.95 (m, 8H, C₆H₄—C₆H₄), 4.20 (br s, 14H, C₅H₅, C₅H₄), 4.44, 4.52 (d, 4H, C₅H₄). ¹³C NMR (DCCl₃, δ): 199.38 (CO), 127.25, 128.75, 130.20, 138.01, 138.29, 139.40, 139.97 (C₆H₄—C₆H₄), 85.18, 90.78, 92.36,93.37 (C=C), 69.40, 69.68, 70.10 (Cp). MS (FAB, relative abundance): 1059 (M⁺-3CO, 24%), 1031 (M⁺-4CO, 8%), 1003 (M⁺-5CO, 3%), 976 (M⁺-6CO, 6%).

Complex **13**: Anal. Calc. for $C_{48}H_{25}Co_4Fe_2NO_{14}$: C, 48.53; H, 2.11; N, 1.18. Found: C, 48.05; H, 2.35; N, 1.23%. IR (KBr disk), v(CO): 2080 (s), 2049 (vs), 2013 (vs) cm⁻¹. ¹H NMR (DCCl₃, δ): 7.26-8.48 (m, 7H, $C_6H_3-C_6H_4$), 4.19, 4.25 (2s, 14H, C_5H_5 , C_5H_4), 4.45, 4.49, 4.52 (t, 4H, C_5H_4). ¹³C NMR (DCCl₃, δ): 198.80, 199.29 (CO), 92.38, 92.72, 123.90, 128.34, 129.99, 132.69, 133.83, 134.73, 136.28, 139.36, 140.43, 149.18 ($C_6H_3-C_6H_4$), 84.23, 85.07, 86.75, 90.53 (C=C), 69.42, 69.68, 69.80, 70.01, 70.15 (Cp). MS (FAB, relative abundance): 733 (M⁺-12CO-2Co, 7%), 615 [M⁺-Co₄(CO)₁₂, 12%].

Complex 14: Anal. Calc. for C₄₄H₂₂Co₄FeO₁₂: C. 51.06: H, 2.13. Found: C, 50.51; H, 1.97%. IR (KBr disk), v(CO): 2085 (s), 2049 (vs), 2018 (vs) cm⁻¹. ¹H NMR $(DCCl_3, \delta)$: 7.21–7.96 (m, 8H, C₆H₄–C₆H₄, C₆H₅), 4.19, 4.21 (2s, 5H, C₅H₅), 4.26 (br s, 1H, C₅H₄), 4.44, 4.53 $(2t, 3H, C_5H_4)$. ¹³C NMR (DCCl₃, δ): 199.43, 199.23 (CO), 126.82, 127.26, 127.37, 127.45, 127.95, 128.40, 128.73, 129.03, 129.27, 129.81, 130.27, 131.64, 132.21, 137.81, 138.13, 138.32, 139.82, 139.92 (C₆H₄-C₆H₄, C₆H₅), 85.80, 90.06 (C=C), 69.41, 69.70, 70.01, 70.17 (Cp). MS (FAB, relative abundance): 1034 (M⁺, 8%), 978 (M⁺-2CO, 18%), 866 (M⁺-6CO, 37%), 810 $(M^{+}-8CO.)$ 39%), 754 (M⁺-10CO, 698 10%). (M⁺-12CO, 4%), 580 (M⁺-12CO-2Co, 7%), 462 $(M^+-12CO-4Co, 7\%).$

2.6. X-ray crystallography of compounds 1, 4, 8, 9 and 11

Black crystals of compounds 1, 4, 8, 9 and 11 were mounted on a glass fibres. All measurements were made on Bruker SMART APEX CCD diffractometers with graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. All data were collected at 20 °C using the ϕ and ω scan techniques. All structures were solved by direct methods and expanded using a Fourier technique [20]. An absorption correction based on SADABS was applied [21]. All non-hydrogen atoms were refined by full matrix least-squares on F^2 . Hydrogen atoms were located and refined by a geometry method. The cell refinement, data collection and reduction were done by Bruker SMART and SAINT programs [22]. The solution and refinement of the structures were performed by SHELXSL97 [23].



 $R = C_6H_4 - C_6H_4 - I(2), C_6H_4 - C_6H_4 - NO_2(3), C_6H_3(NO_2) - C_6H_4I(4)$



 $\mathsf{R}^{"}=\mathsf{Fc},\ \mathsf{R}^{'}=\mathsf{C}_{6}\mathsf{H}_{4}\text{-}\mathsf{C}_{6}\mathsf{H}_{4}\ (5),\ \mathsf{C}_{6}\mathsf{H}_{3}(\mathsf{NO}_{2})\text{-}\mathsf{C}_{6}\mathsf{H}_{4}\ (6);\ \ \mathsf{R}^{"}=\mathsf{C}_{6}\mathsf{H}_{5},\ \mathsf{R}^{'}=\mathsf{C}_{6}\mathsf{H}_{4}\text{-}\mathsf{C}_{6}\mathsf{H}_{4}\ (7)$



 $\mathsf{R} = \mathsf{C}_{6}\mathsf{H}_{4}\text{-}\mathsf{C}_{6}\mathsf{H}_{5} \text{ (8), } \mathsf{C}_{6}\mathsf{H}_{4}\text{-}\mathsf{C}_{6}\mathsf{H}_{4}\text{-}\mathsf{I} \text{ (9), } \mathsf{C}_{6}\mathsf{H}_{4}\text{-}\mathsf{NO}_{2} \text{ (10), } \mathsf{C}_{6}\mathsf{H}_{3} (\mathsf{NO}_{2})\text{-}\mathsf{C}_{6}\mathsf{H}_{4}\mathsf{I} \text{ (11)}$



$$R'' = Fc, R' = C_6H_4-C_6H_4$$
 (12), $C_6H_3(NO_2)-C_6H_4$ (13); $R'' = C_6H_5, R' = C_6H_4-C_6H_4$ (14)

Scheme 2.

Table 3 Crystal data and relevant structural parameters of compounds **1**, **4**, **8**, **9** and **11**

Compounds	1	4	8	9	11
Empirical formula	C ₂₄ H ₁₈ Fe	C ₂₄ H ₁₆ FeINO ₂	C ₃₀ H ₁₈ Co ₂ FeO ₆	C ₃₀ H ₁₇ Co ₂ FeIO ₆	C ₃₀ H ₁₆ Co ₂ FeINO ₈
Crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	P2(1)/c	$P\overline{I}$	$P\overline{I}$	P2(1)/n	P2(1)/c
a (Å)	11.585(3)	9.198(4)	9.963(7)	10.240(4)	8.708(3)
$b(\mathbf{A})$	7.3723(19)	11.899(5)	15.111(11)	22.047(8)	23.492(9)
c (Å)	20.928(6)	18.935(8)	19.554(14)	12.559(5)	14.813(5)
α (°)	90.00	83.676(6)	71.002(11)	90	90
β (°)	101.345(5)	89.663(6)	87.090(12)	98.728(4)	98.691(6)
γ (°)	90.00	82.237(7)	79.626(13)	90	90
Volume, Z	1752.5(8), 4	2040.8(14), 4	2738(3), 4	2802.6(18), 4	2995.4(19), 4
$D_{\rm calc} ({\rm g/cm}^3)$	1.373	1.735	1.572	1.835	1.816
$\mu (\mathrm{mm}^{-1})$	0.862	2.272	1.762	2.825	2.654
<i>F</i> (000)	752	1048	1304	1512	1600
θ Range (°)	1.79-25.01	3.127-25.24	1.10-25.01	1.85-26.01	1.64-25.01
Reflections collected	7020	8555	11600	12767	12454
Independent reflections	3088	7052	9507	5523	5259
Completeness to θ (%)	99.7	98.2	98.5	99.9	99.7
Maximum and minimum transmission	0.9342 and 0.8465	0.8047 and 0.6593	0.8719 and 0.7780	0.8056 and 0.6020	0.7772 and 0.5567
Data/restraints/parameters	3088/0/226	7052/0/523	9507/0/703	5523/0/361	5259/0/388
Goodness-of-fit	0.955	0.933	0.842	0.930	1.033
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	R_1 , 0.1081; wR_2 , 0.1047	R_1 , 0.0446; wR_2 , 0.1059	R_1 , 0.0551; wR_2 , 0.1138	R_1 , 0.0304; wR_2 , 0.0665	R_1 , 0.0688; wR_2 , 0.1493
R-indices (all data)	R_1 , 0.2561; wR_2 , 0.1333	R_1 , 0.0656; wR_2 , 0.1132	R_1 , 0.1207; wR_2 , 0.1422	$R_1, 0.0444, wR_2, 0.0708$	$R_1, 0.1046, wR_2, 0.1666$
Largest difference in peak and hole $(e \text{ Å}^{-3})$	0.331 and -0.313	0.627 and -1.015	0.713 and -0.384	0.642 and -0.562	1.599 and -0.958

3. Results and discussion

3.1. Syntheses and characterizations of the ferrocenylacetylenylbiphenyl derivatives and their complexes

The coupling reactions carried out in this work are summarized in Scheme 1. The addition reactions of the ligands Fc-C = C - R and Fc-C = C - R' - C = C - R'' with $Co_2(CO)_8$ are summarized in Scheme 2. The complexes **8**, **9**, **10**, **11**, **12**, **13** and **14** were prepared by the addition reaction between the Co-Co bond of $Co_2(CO)_8$ and the C=C triple bond of the ligands Fc-C = C - R and Fc-C = C - R' - C = C - R''



Fig. 1. Molecular structure of compound 1.



Fig. 2. Molecular structure of compound 4.

with the mole ratios of $Co_2(CO)_8$ to ligand fixed at 1:1 and 1:2, respectively. The compounds are yellow for 1 and 2 and orange for 3, 4, 5, 6 and 7, and they are air-stable crystalline compounds which are slightly soluble in non-polar solvents such as hexane, and easily soluble in benzene and polar solvents such as dichloromethane. The complexes 8–14 are black crystals and their solubilities are similar to the corresponding ligands. The IR spectra (2077–2018 cm⁻¹) confirm that there are coordinated $Co_2(CO)_6$ species with C=C triple bonds in complexes 8–14. The compositions and structures of compounds 1–14 are further proved by the data of their element analyses, ¹H, ¹³C NMR and MS.

3.2. Molecular structures of compounds 1, 4, 8, 9 and 11

The molecular structures of compounds 1, 4, 8, 9, 11 were determined by X-ray single crystal analysis. Crystal data and relevant structural parameters are enumerated in Table 3. The structures of compounds 1, 4, 8, 9 and 11, with the atom numbering scheme, are shown in Figs. 1–5, respectively, and selected bond lengths and angles are listed in Table 4.

The molecules of compounds 1, 4, 8, 9 and 11 are constituted of a π -conjugated alkynyl system with terminal ferrocenyl and biphenyl or substituted biphenyl units, respectively. In 1 the bond distance C(11)–C(12) (1.183 Å) shows there is a carbon–carbon triple bond. The bond distances C(10)–C(11) (1.45 Å) and C(12)– C(13) (1.44 Å) are shorter than that of C(16)–C(19) (1.51 Å) as a result of stronger electron delocalization



Fig. 4. Molecular structure of compound 9.



Fig. 3. Molecular structure of compound 8.



Fig. 5. Molecular structure of compound 11.

between the C \equiv C bond (sp-C) and biphenyl (sp²-C) or the C \equiv C bond (sp-C) and ferrocenyl group (sp²-C) than that between two phenyl groups (two sp^2 -C). The bond angle data in Table 2 demonstrate that the linear structure of compound 1 is altered to a non-linear structure in 8. while the alkyne bond of 1 is coordinated to a $Co_2(CO)_6$ unit. The molecular structures of compounds 4 and 11 are similar to the structures of compounds 1 and 8, respectively (see Figs. 2, 5 and 1, 3). The coordinated $Co_2(CO)_6$ units with the C \equiv C bond in complexes 8, 9 and 11 are all approximately tetrahedral u-alkyne dicobalt moieties. The alkyne bond adopts a typical $\mu_2 - \eta^2$ coordination fashion with the alkyne bond lying essentially perpendicular to the Co-Co bond in the C₂Co₂ unit. The average Co-Co bond distance (2.46 Å) is typical of classical alkyne dicobalt complexes. The average C-C bond length (1.34 Å) of the C₂Co₂ fragments shows a bond distance of the coordinated C \equiv C bond located in the scope of a C-C double bond. In complexes 8, 9 and 11 the $Co_2(CO)_6$ units coordinated to the alkyne bond are in a trans configuration with the biphenyl and ferrocenyl groups, and the two terminal groups (biphenyl or substituted biphenyl and ferrocenyl groups) are orientated cis to each other (see Fig. 3-5).

In compounds 1, 4, 8, 9 and 11, the data of the dihedral angles (40.12° for 1, 52.52° for 4, 26.30° for 8, 35.41° for 9 and 57.51° for 11) between the two phenyl rings are different from each other, and have been affected by the substituted group on the biphenyl ring and the coordinated $Co_2(CO)_6$ unit with the alkyne. The dihedral angle between the two phenyl rings in 1 is smaller than that in 4 because of the effect of the substituted group (NO₂) on the phenyl

ring. The data of the dihedral angles $(1.97^{\circ} \text{ for } 1, 0.88^{\circ} \text{ for } 4, 4.01^{\circ} \text{ for } 8, 5.58^{\circ} \text{ for } 9 \text{ and } 2.97^{\circ} \text{ for } 11)$ between the two Cp planes in compounds 1, 4, 8, 9 and 11 reveal that the two Cp planes are nearly parallel in 4, but are slightly deviated from parallel in 1, 8, 9 and 11.

3.3. Electrochemical properties of compounds 1–12

The electrochemical properties of compounds 1-12 have been studied by cyclic voltammetry at 298 K in a standard three-electrode system with *n*-NBu₄ClO₄(TBAP) in CH₂Cl₂ solution as the supporting electrolyte. The results are given in Table 5.

For compounds 1-7 and complexes 8, 10 and 12 the usual electrochemically quasi-reversible ferrocene (0/1+)peak couples and a one-electron redox process were observed (see Table 1), but for complexes 9 and 11 an irreversible redox process was observed. Only a pair of redox peaks appears, which reveals that there are no Fe-Fe interactions in the di-ferrocenyl compounds 5, 6 and 12 through the conjugated biphenyl ethynyl bridges [17]. However, a redox behavior study of ethynyl-bridged ferrocenes, such as the Fc-(C=C)₂-Fc ligand and its clusters, demonstrates two one-electron redox processes, which show there are Fe-Fe interactions [24]. The irreversible reduction peaks within range $E_{pc} = -0.55$ to -0.88 V in complexes 8–12 were regarded as the result of a reducing process on the $Co_2(CO)_6$ moieties. Although there are substituted electron-withdrawing groups on the biphenyl rings in compounds 2, 3, 4, 6, 9, 10 and 11, and the coordinated $Co_2(CO)_6$ units for complexes 8–12, no significant variation of E^0 was observed.

Table 4 Selected bond lengths (Å) and angles (°) for $1,\,4,\,8,\,9$ and 11

Bond lengths				Bond angles			
1							
C(10)–C(11)	1.45(1)	C(12)-C(13)	1.44(1)	C(10)-C(11)-C(12)	179.2(1)	C(15)-C(16)-C(19)	120.3(8)
C(11)–C(12)	1.18(1)	C(16)-C(19)	1.51(1)	C(11)-C(12)-C(13)	177.6(1)	C(16)-C(19)-C(20)	120.8(1)
4							
C(10)–C(11)	1.44(6)	C(12)-C(13)	1.44(6)	C(10)-C(11)-C(12)	178.3(5)	C(17)-C(16)-C(19)	123.3(4)
C(11)-C(12)	1.18(6)	C(16)-C(19)	1.48(6)	C(11)-C(12)-C(13)	176.5(5)	C(16)-C(19)-C(24)	121.6(4)
8							
C(11)–C(12)	1.44(9)	Co(1)–C(12)	1.99(7)	C(11)-C(12)-C(13)	145.9(6)	Co(1)–C(12)–C(13)	68.6(4)
C(12)–C(13)	1.33(8)	Co(1)–C(13)	1.95(7)	C(12)-C(13)-C(14)	144.5(7)	Co(1)-C(13)-C(12)	71.9(4)
C(13)-C(14)	1.46(8)	Co(2)-C(12)	1.96(6)	C(13)-C(14)-C(15)	122.0(6)	Co(2)–C(12)–C(13)	70.5(4)
Co(1)–Co(2)	2.46(2)	Co(2)-C(13)	1.97(6)	C(18)-C(17)-C(20)	121.6(6)	Co(2)-C(13)-C(12)	69.7(4)
9							
C(16)–C(17)	1.45(4)	Co(1)–C(17)	2.00(3)	C(16)-C(17)-C(18)	144.2(3)	Co(1)-C(17)-C(18)	68.2(2)
C(17)–C(18)	1.33(4)	Co(1) - C(18)	1.94(3)	C(17)-C(18)-C(19)	141.9(3)	Co(1)-C(18)-C(17)	72.4(2)
C(18)–C(19)	1.46(4)	Co(2)–C(17)	1.95(3)	C(18)-C(19)-C(20)	122.2(3)	Co(2)–C(17)–C(18)	71.8(2)
Co(1)-Co(2)	2.46(8)	Co(2)-C(18)	1.99(3)	C(21)-C(22)-C(25)	120.9(3)	Co(2)-C(18)-C(17)	68.7(2)
11							
C(10)–C(11)	1.44(1)	Co(1)–C(11)	2.01(7)	C(10)-C(11)-C(12)	144.8(7)	Co(1)–C(11)–C(12)	68.6(4)
C(11)–C(12)	1.34(1)	Co(1)–C(12)	1.97(7)	C(11)-C(12)-C(19)	141.5(7)	Co(1)-C(12)-C(11)	72.1(4).
C(12)–C(19)	1.45(9)	Co(2)–C(11)	1.96(7)	C(12)-C(19)-C(20)	120.5(7)	Co(2)–C(11)–C(12)	70.6(4)
Co(1)-Co(2)	2.46(2)	Co(2)-C(12)	1.97(7)	C(22)-C(25)-C(26)	121.8(7)	Co(2)–C(12)–C(11)	69.5(4)

Table 5 Voltammetric data^a

Compound	$E_{\rm pc}$	$E_{\rm pa}$	$i_{\rm pc}/i_{\rm pa}$	$E^{0}(0/1+)$	Reduction of Co, $E_{\rm pc}$
1	0.33	1.28	0.96	0.81	
2	0.36	1.19	1.01	0.78	
3	0.44	1.21	0.82	0.83	
4	0.42	1.19	0.93	0.81	
5	0.34	1.50	1.00	0.92	
6	0.35	1.40	1.00	0.88	
7	0.36	1.24	1.04	0.80	
8	0.34	1.40	0.99	0.87	-0.72
9	0.37	1.09	0.19	0.73	-0.58
10	0.37	1.21	0.92	0.79	-0.88
11	0.48	1.10	0.21	0.79	-0.55
12	0.26	1.37	0.89	0.82	-0.77

 $E_{\rm pc}$ = cathodic peak potential (V); $E_{\rm pa}$ = anodic peak potential (V); $i_{\rm pc}$ = cathodic peak current (A); $i_{\rm pa}$ = anodic peak current (A); $E^0 = 1/2(E_{\rm pc} + E_{\rm pa})$ (V).

^a Platinum electrode (Ag/Ag⁺ standard) in a 0.001 M n-Bu₄N-ClO₄(TBAP) solution (CH₂Cl₂) at 20 °C with a 100 mV scan rate.

4. Conclusion

Ferrocenylacetylenylbiphenyl and bisferrocenylacetylenyl-biphenyl derivatives could be synthesized by Sonogashira coupling and a second Sonogashira coupling reaction, respectively, and their cobalt coordinated complexes could be obtained by the addition reaction of $Co_2(CO)_6$ units to the alkyne bond. The molecular structures of complexes 8, 9 and 11 show the $Co_2(CO)_6$ units coordinated to the alkyne bond are in a trans configuration with the terminal biphenyl derivatives and ferrocenyl groups. The data of dihedral angles reveal two phenyl rings of biphenyl derivatives in compounds 1, 4, 8, 9 and 11 are deviated from parallel.

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Appendix A. Supplementary material

CCDC 625423, 625424, 625425, 625426 and 625427 contain the supplementary crystallographic data for **1**, **8**, **4**, **11** and for **9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.02.023.

References

- [1] W.Y. Wong, Coord. Chem. Rev. 249 (2005) 971.
- [2] L.B. Gao, L.Y. Zhang, L.X. Shi, Z.N. Chen, Organometallics 24 (2005) 1678.
- [3] T.Y. Dong, S.W. Chang, S.F. Lin, M.C. Lin, Y.S. Wen, L.S. Lee, Organometallics 25 (2006) 2018.
- [4] N. Duffy, J. McAdam, C. Nervi, D. Osella, M. Ravera, B. Robinson, J. Simpson, Inorg. Chim. Acta 247 (1996) 99.
- [5] D. Osella, L. Milone, C. Nervi, M. Ravera, Eur. J. Inorg. Chem. (1998) 1473.
- [6] J. McAdam, J.J. Brunton, B.H. Robison, J. Simpson, J. Chem. Soc., Dalton Trans. (1999) 2487.
- [7] R.D. Stephens, C.E. Castro, J. Org. Chem. 28 (1963) 3313.
- [8] M. Rosenblum, N. Brawn, J. Papenmeier, M. Applebaum, J. Organomet. Chem. 6 (1966) 173.
- [9] H. Nock, H. Schottenberger, J. Org. Chem. 58 (1993) 7045.
- [10] R.P. Hsung, C.E.D. Chidsey, L.R. Sita, Organometallics 14 (1995) 4808.
- [11] A. Arques, D. Aunon, P. Molina, Tetrahedron Lett. 45 (2004) 4337.
- [12] P.F.H. Schwab, J.R. Smith, J. Michl, Chem. Rev. 105 (2005) 1197.
- [13] H. Lang, R. Packheiser, B. Wolfort, Organometallics 25 (2006) 1836.
- [14] I.P. Beletskaya, A.V. Tsvetkov, G.V. Latyshev, V.A. Tafeenko, N.V. Lukashev, J. Organomet. Chem. 637-639 (2001) 653.
- [15] F. Alonso, I.P. Beleskaya, M. Yus, Chem. Rev. 104 (2004) 3079.
- [16] E. Lindner, R. Zong, K. Eichele, M. Strobele, J. Organomet. Chem. 660 (2002) 78.
- [17] N. Chawdhury, N.J. Long, M.F. Mahon, L.L. Ooi, P.R. Raithby, S. Rooke, A.J.P. White, D.J. Williams, M. Younus, J. Organomet. Chem. 689 (2004) 840.
- [18] V.H.O. Wirth, O. Konigstein, W. Kern, J. Liebigs Ann. Chem. 634 (1960) 83.
- [19] A.H. Hobukob, Zhurnal Obshchei Khimii 29 (1959) 58.
- [20] G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467.
- [21] G.M. Sheldrick, SADABS, Siemens Area Detector Absorption, Correction Software, University of Göttingen, Germany, 1997.
- [22] Bruker, SMART and SAINT, Area Detector Control and Integration Software, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1998.
- [23] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Analysis, University of Göttingen, Germany, 1997.
- [24] R.D. Adams, B. Qu, M.D. Smith, T.A. Albright, Organometallics 21 (2002) 2970.