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Photolytic reaction of substituted (ethynyl)benzaldehyde and $Fe(CO)_5$: Formation of indenone and chelated iron complexes

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ABSTRACT

At 0 °C, photolysis of a hexane solution containing $Fe(CO)_5$ and 2-(phenylethynyl)benzaldehyde (**1**) affords a mixture of mononuclear (tricarbonyliron-2-phenylindenone, (**2**) and binuclear acetylene coupled iron carbonyl complexes $[Fe(CO)_3\{\eta^4\text{-}2,4-(C_6H_4CHO)_2-3,5\text{-}(C_6H_5)_2C_4\}Fe(CO)_3]$, **3**, $[Fe(CO)_3\{\ \eta^4\text{-}2\text{-}(\eta^1-C_6H_4CHO)-4-(C_6H_4CHO)-3,5\text{-}(C_6H_5)_2C_4\}Fe(CO)_2]$, **4** and $[Fe(CO)_3\{\ \eta^4\text{-}4\text{-}(\eta^1\text{-}2-C_6H_4CHO)-2-(C_6H_4CHO)-3,5\text{-}(C_6H_5)_2\ C_4\}Fe(CO)_2]$, **5**. In compounds **4** and **5**, the exocyclic iron atom is η^4-bonded with the ferracyclopentadiene unit, and it bears two terminal carbonyls. Its 18 electron count is completed by virtue of the aldehydic oxygen atom coordinating to the iron atom. Photolysis of 2-(ferrocenylethynyl)benzaldehyde (**6**) under similar condition leads to the formation of tricarbonyliron-2-ferrocenylindenone (**7**) and tetracarbonyl(2-ferrocenyl-3-(2-formylphenyl)maleoyl)iron (**8**) predominantly.

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1. Introduction

Activation of acetylene on transition metal complexes is of considerable importance [1–3]. Reactions of iron pentacarbonyl with mono or diacetylenes result in the formation of mononuclear and/or dinuclear ironcarbonyl complexes along with some acetylene coupled and CO inserted organic products [4–12]. In our previous reports, we have shown the formation of quinones from the photochemical reaction of different acetylenes using iron pentacarbonyl [4,5,13,14]. Recently, we have reported the role of iron pentacarbonyl in the formation of α,β-vinylesters and alkoxy substituted γ-lactones under photochemical condition [15]. We have extended our investigation on the effect of formyl group in ortho phenylethynylbenzaldehyde towards the complex formation by iron pentacarbonyl. It has been observed that η^2 form of bonding of the formyl group is preferred when the metallic part [M] is a d^{10} ML_2 fragment ($Pt(PR_3)_2$ [16,17], $Pd(PR_3)_2$ [18], $Ni(PR_3)_2$ [19–21]) or a C_{2v} d^8 ML_4 fragment ($Os(CO)_2(PR_3)_2$ [22], $Ru(CO)_2(PR_3)_2$ [23,24], $Fe(CO)_2(PR_3)_2$ [25]) while the η^1 form is preferred when [M] is a d^8 ML_3 fragment ($PtCl_2$(pyridine) [26,27], $Pt^+CH_3(PR_3)_2$ [28]), an octahedral d^6 ML_5 fragment ($(RuCOCl(PR_3)_2$, $SnCl_3$ [29], $Mn_2(CO)_9$ [30]), or a d^6 $CpML_2$ fragment ($CpFe^+(CO)_2$ [31,32]). Some exceptions occur for the d^6 ML_5 $[Os(NH_3)_5]^{2+}$ fragment, the coordination is η^2 [33,34] and, in the case of the d^6 $CpRe^+NO(PR_3)$ fragment, the coordination is η^1 for ketones [35] and η^2 for aldehydes [36,37] as in the case of $CpRe(CO)_2$ [38]. In such complexes, the two forms can coexist with a η^2/η^1 ratio depending on the substituents [39].

There are several reports on the method of synthesis of indenone [40–48]. However, to the best of our knowledge there is no report of their synthesis using ironpentacarbonyl. Indenones are useful intermediates [41] in the synthesis of a variety of molecules, including the C-nor D-homosteroid ring system [49], photochromic indenone oxides [50], 2,4- and 3,4-disubstituted-1-naphthols [51], gibberellines [52], indanones [53] and indanes [54], a building block of many natural products [55]. Use of substituted indenone for the complex formation with $Fe_3(CO)_{12}$ was first reported by Braye and Hübel in 1965 [56]. In this communication we report a reaction of 2-(phenylethynyl)benzaldehyde and 2-(ferrocenylethynyl)benzaldehyde with iron pentacarbonyl under photochemical conditions to form $Fe(CO)_3$ coordinated indenone which underwent oxidative demetallation to yield the free indenone and demonstrated activation of acetylene using simple metal carbonyl under facile condition.

2. Results and discussion

When hexane solution containing 2-(phenylethynyl)benzaldehyde (**1**) and $Fe(CO)_5$ was photolysed under continuous bubbling of

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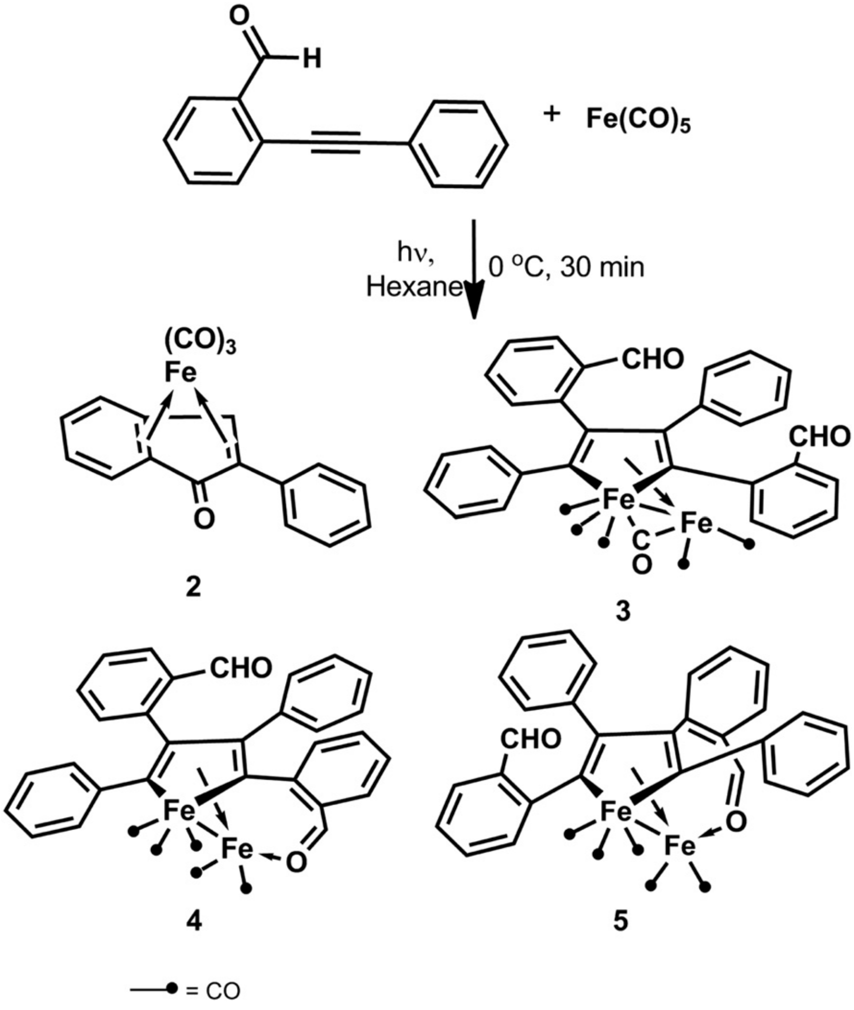
argon at 0 °C for 30 min, formation of compounds **2**–**5** was observed (Scheme 1). These compounds were found to be stable in solid state and characterized by IR and NMR spectroscopy. Suitable single crystals of **2**–**5** were grown from hexane/dichloromethane solvent mixture and their structures were established crystallographically.

IR spectra of compounds **2**–**5** show the presence of terminal carbonyls. In compound **2** the ν(C=O) aldehyde peak is shifted from 1691 to 1625 cm^{-1}, which is also observed in tricarbonylcyclopentadienoneiron complexes, indicative of an increased polarity of the ketonic group.

The molecular structure of compound **2** (Fig. 1) consists of a 2-phenylindenone ring. The five-membered ring is coordinated to a $Fe(CO)_3$ unit in an η^4- fashion. A compound similar to **2**, has been synthesised by Braye and Hübel by the thermal reaction of bis(*p*-chlorophenyl)acetylene with $Fe_3(CO)_{12}$ [56], however, its crystal structure was not established. It is suggested that the phenyl ring of the indenone retains its aromaticity as the tricarbonylironindenone does not participate in Diels–Alder cycloaddition reaction. Unequal C–C bond lengths of the phenyl ring of the indenone unit of **2** (C5–C10 = 1.422(2), C5–C6 = 1.424(2), C6–C7 = 1.342(3), C7–C8 = 1.429(3), C8–C9 = 1.348(3), C9–C10 = 1.424(2) Å) indicates a partial localization of π-electron density in phenyl ring. Also, the CO of indenone is found 7.5° above the plane of indenone ring. This is probably due to weak interaction of oxygen (O1) with C–H hydrogen atoms (H11 and H9) of another molecule in the vicinity; the distances O1 to H11, 2.369 Å and O1 to H9, 2.559 Å are less than the sum of Vander Waals radii of two atoms.

Compounds **3**, **4** and **5** belong to the class of (1,1,1-tricarbonylferraindene)-π-carbonyliron complexes [56]. In compound **3** (Fig. 2), a ferracyclopentadiene ring is formed by the coupling of two units of 2-(phenylethynyl)benzaldehyde and insertion of ironcarbonyl. The ring is substituted with formylphenyl group at 1 and 3–carbon positions and with phenyl group at 2 and 4–carbon positions. The ferracyclopentadiene ring is bonded to another $Fe(CO)_3$ unit in an η^4 fashion which is reflected by almost similar bond distances for C14–C15 = 1.423(7), C15–C29 = 1.435(7) and C29–C30 = 1.410(7) in the ring plane. This $Fe(CO)_3$ unit is in turn bonded to the cyclic Fe through an Fe–Fe bond. One carbonyl group semi-bridges between Fe1 and Fe2, where Fe1–C1–O1 bond angle is 159.9(7)°.

ORTEP diagrams of compound **4** and **5** as have shown in Figs. 3 and 4 respectively show them to be chelated iron complexes and isomers. The infrared spectra of these compounds show an additional ν(C=O) peak at 1729 and 1720 cm^{-1} respectively. The ferracyclopentadiene ring is bonded to two formylphenyl groups at 2 and 4–carbon positions and to two phenyl groups at 3 and 5–carbon positions. This ferracyclopentadiene ring is coordinated in η^4 fashion to another $Fe(CO)_2$ unit. In both compounds, the oxygen atom of one of the formylphenyl unit coordinates to the



Scheme 1. Photolysis of 2-(phenylethynyl)benzaldehyde with $Fe(CO)_5$.

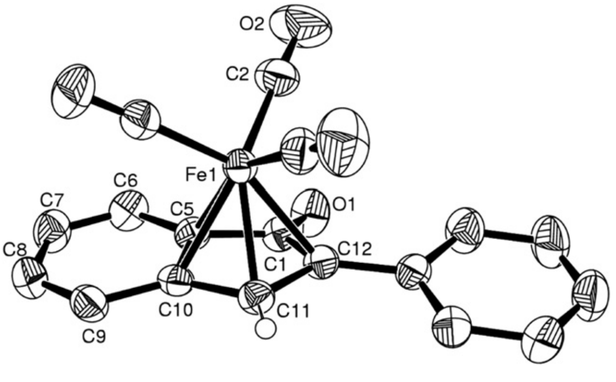


Fig. 1. ORTEP diagram of compound 2 with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): C1−C5 = 1.477(2), C1−C12 = 1.482(2), C5−C10 = 1.422(2), C5−C6 = 1.424(2), C6−C7 = 1.342(3), C7−C8 = 1.429(3), C8−C9 = 1.348(3), C9−C10 = 1.424(2), C10−C11 = 1.425(2), C11−C12 = 1.439(2),; O2−C2−Fe1 = 177.85(19), O3−C3−Fe1 = 178.01(18), O4−C4−Fe1 = 178.6(2), C5−C10−C11 = 108.03(15), C10−C11−C12 = 108.79(15), C11−C12−C1 = 107.96(15), C5−C1−C12 = 103.89(14), C10−C5−C1 = 109.09(15).

exocyclic iron atom whereas in **4** the coordinated formylphenyl substituent in the ferracyclopentadiene unit is adjacent to the iron atom in the ring, in **5**, it is at position 4. It is known that the mode of bonding of the aldehydic group as η^1 or η^2 depends on electronic environment around the metal atom; η^1 being preferred when the metal fragment to which it is bonded has electron withdrawing capabilities [57]. The CO bonded iron centre is sufficiently electron withdrawing in nature favouring η^1 coordination of aldehydic group and this is also supported by the crystal structure where there is no significant difference between the bond lengths of free and the coordinated aldehydic C−O bond.

In compound **3**, the formyl group is not coordinated to the exocyclic iron and one of the carbonyl groups semi-bridges between two iron atoms. Since aldehydic oxygen is a σ donor and not a π acceptor like carbonyl, electron density is more on the exocyclic iron which in turn increases the electron density on the endocyclic iron atom. Therefore, the semibridging character is less

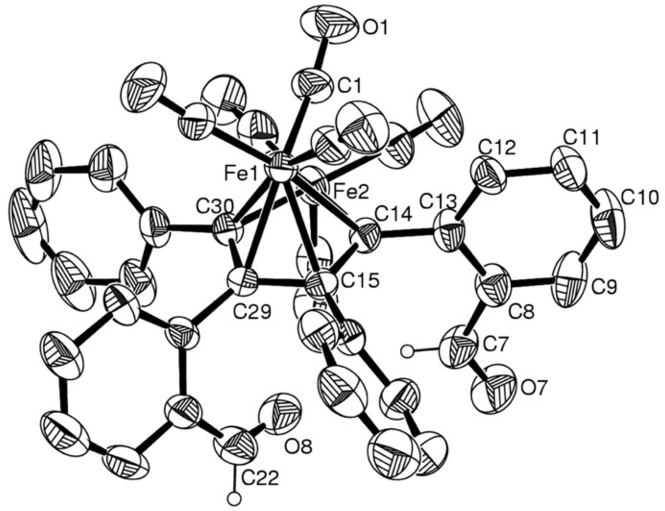


Fig. 2. ORTEP diagram of compound 3 with 30% probability ellipsoids. Solvent molecule is removed for clarity. Selected bond lengths (Å) and bond angles (deg): Fe1−C1 = 1.780(6), Fe1−C29 = 2.162(5), Fe1−C30 = 2.100(5), Fe1−C14 = 2.119(5), Fe1−C15 = 2.154(5), Fe1−Fe2 = 2.4902(12), Fe2−C1 = 2.357(7), Fe2−C14 = 1.985(6), Fe2−C30 = 1.967(5), C14−C15 = 1.423(7), C15−C29 = 1.435(7), C29−C30 = 1.410(7); O1−C1−Fe1 = 159.9(7), O1−C1−Fe2 = 127.6(6), O2−C2−Fe1 = 176.7(6), O3−C3−Fe1 = 176.2(6), O4−C4−Fe2 = 175.1(8), O5−C5−Fe2 = 178.8(8), O6−C6−Fe2 = 178.9(8), C1−Fe1−Fe2 = 64.5(2), C1−Fe2−Fe1 = 42.96(16), C30−Fe2−C14 = 80.2(2), C15−C14−Fe2 = 117.0(4), C14−C15−C29 = 111.1(5), C30−C29−C15 = 115.0(4), C29−C30−Fe2 = 115.7(4).

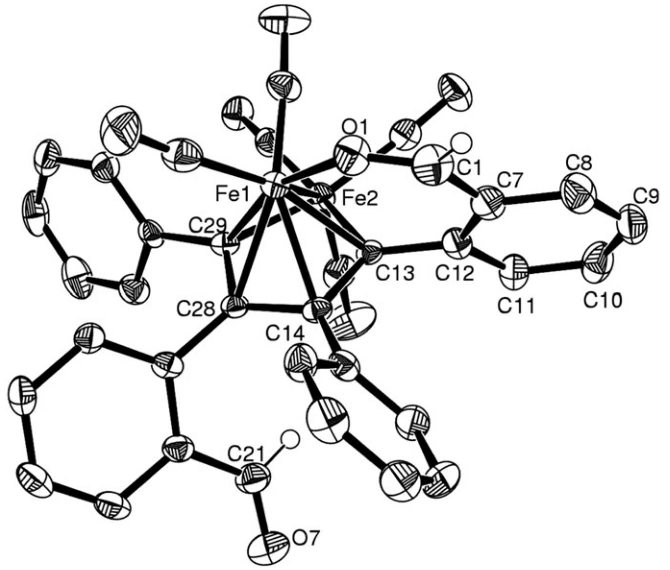


Fig. 3. ORTEP diagram of compound 4 with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Fe1−C3 = 1.764(4), Fe1−C2 = 1.784(4), Fe1−O1 = 1.991(2), Fe1−C13 = 2.066(3), Fe1−C14 = 2.119(3), Fe1−C28 = 2.162(3), Fe1−C29 = 2.067(3), Fe1−Fe2 = 2.4916(7), Fe2−C13 = 1.952(3), Fe2−C29 = 1.972(3), O1−C1 = 1.234(4), O7−C21 = 1.209(4), C13−C14 = 1.445(4), C14−C28 = 1.429(5), C28−C29 = 1.423(5), C1−C7 = 1.429(6), C7−C12 = 1.408(5), C12−C13 = 1.467(5); C1−O1−Fe1 = 130.1(2), O1−C1−C7 = 128.6(3), O7−C21−C22 = 124.9(4), O2−C2−Fe1 = 176.3(4), O3−C3−Fe1 = 169.4(3), O4−C4−Fe2 = 175.6(3), O5−C5−Fe2 = 177.8(4), O6−C6−Fe2 = 175.6(3), C13−Fe2−C29 = 80.26(13), C14−C13−Fe2 = 116.9(2), C28−C14−C13 = 111.9(3), C29−C28−C14 = 113.1(3), C28−C29−Fe2 = 116.1(2), Fe2−Fe1−O1 = 124.2(8).

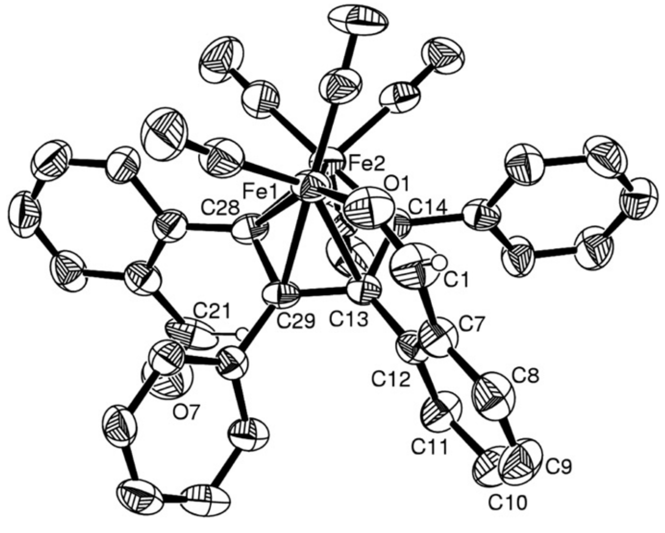
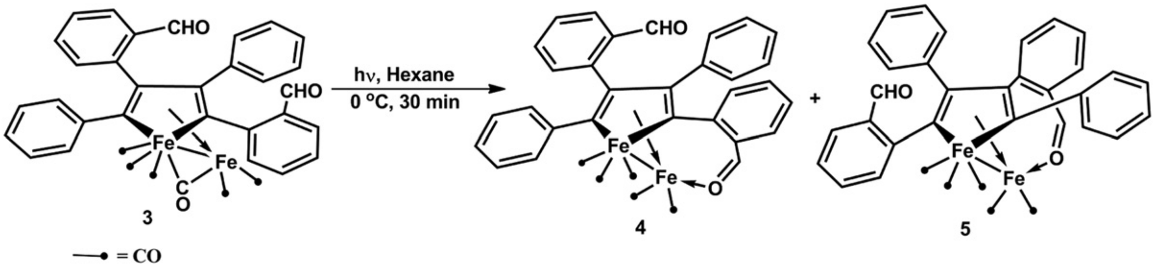
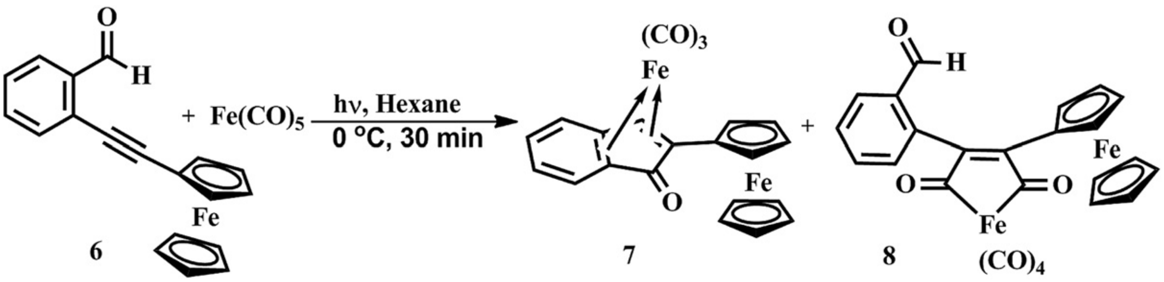


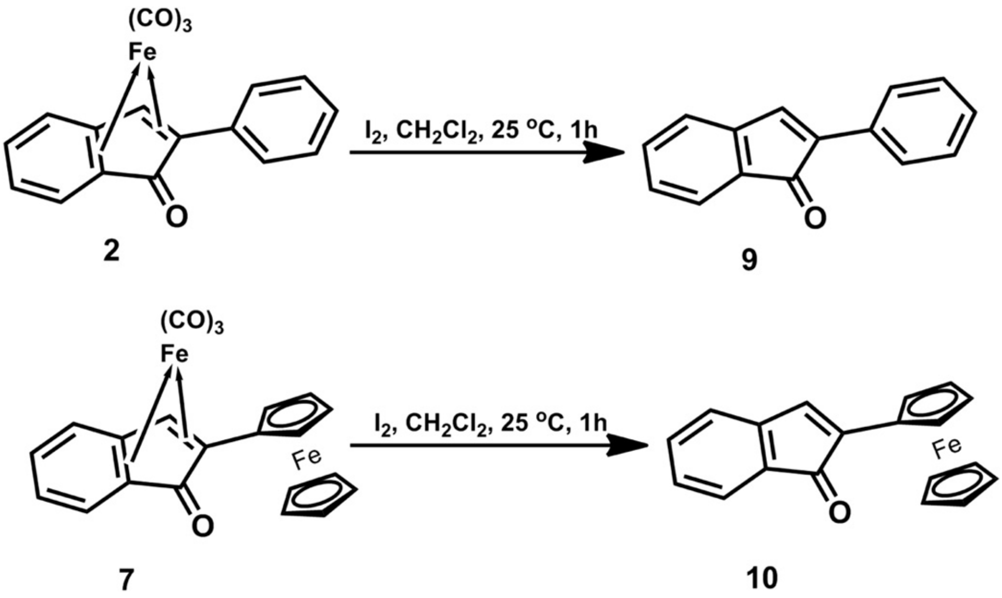
Fig. 4. ORTEP diagram of compound 5 with 30% probability ellipsoids. Solvent molecule is removed for clarity. Selected bond lengths (Å) and bond angles (deg): Fe1−O1 = 2.002(5), Fe1−C2 = 1.770(8), Fe1−C3 = 1.768(7), Fe1−C13 = 2.118(5), Fe1−C14 = 2.110(6), Fe1−C28 = 2.080(6), Fe1−C29 = 2.123(5), Fe1−Fe2 = 2.5063(12), Fe2−C14 = 1.939(5), Fe2−C28 = 1.988(6), O1−C1 = 1.230(8), O7−C21 = 1.195(7), C13−C14 = 1.393(7), C13−C29 = 1.428(8), C28−C29 = 1.454(7); C1−O1−Fe1 = 133.1(5), C12−C13−Fe1 = 124.1(4), O1−Fe1−C13 = 87.39(19),O2−C2−Fe1 = 175.7(7), O3−C3−Fe1 = 173.5(6), O4−C4−Fe2 = 177.5(7), O5−C5−Fe2 = 176.0(7), O6−C6−Fe2 = 177.2(6), C14−C13−C29 = 114.0(5), C13−C14−Fe2 = 117.4(4), C13−C29−C28 = 112.5(5), C29−C28−Fe2 = 114.0(5), C14−Fe2−C28 = 81.1(2), Fe2−Fe1−O1 = 145.4(15).



Scheme 2. Photochemical formation of $[Fe(CO)_3\{\eta^4\text{-}2\text{-}(\eta^1\text{–}C_6H_4CHO)\text{–}4\text{–}(C_6H_4CHO)\text{–}3,5\text{-}(C_6H_5)_2C_4\}Fe(CO)_2]$, **4** and $[Fe(CO)_3\{\eta^4\text{-}4\text{-}(\eta^1\text{-}2\text{–}C_6H_4CHO)\text{–}2\text{–}(C_6H_4CHO)\text{–}3,5\text{-}(C_6H_5)_2C_4\}Fe(CO)_2]$, **5** from $[Fe(CO)_3\{\eta^4\text{-}2,4\text{–}(C_6H_4CHO)_2\text{–}3,5\text{-}(C_6H_5)_2C_4\}Fe(CO)_3]$, **3**.



Scheme 3. Photolysis of 2-(ferrocenylethynyl)benzaldehyde with $Fe(CO)_5$.



Scheme 4. Demetallation of irontricarbonylindenones to respective indenones.

in compounds **4** and **5**. Further, in compound **4**, Fe2–Fe1–O1 bond angle is 124.2(8)° whereas in compound **5**, Fe2–Fe1–O1 bond angle is 145.4(1)°. In compound **5**, the aldehydic oxygen is more trans to endocyclic iron compared to compound **4**, and therefore, the carbonyl group (C3–O3) in **5** has more terminal character (Fe1–C3–O3 = 173.5(6)°) compared to compound **4** (bond angle Fe1–C3–O3 = 169.4(3)°).

Compounds **4** and **5** are considered to be formed from compound **3** by loss of one carbonyl group from $Fe_2(CO)_6$ unit. To confirm this, we photolyzed hexane solution of compound **3** in inert atmosphere, which gives a mixture of compounds **4** and **5**, along with two other minor products, formed in insufficient amounts to enable characterization. (Scheme 2).

Photolysis of 2-(ferrocenylethynyl)benzaldehyde (**6**) and $Fe(CO)_5$ under similar condition results in a mixture of two products, (tricarbonyl(2-ferrocenylindenone)iron) **7** and (tetracarbonyl(3-ferrocenyl-4-(2-formylphenyl)maleoyl)iron) **8**, a ferrole derivative (Scheme 3). Usually, it has been observed that ferrole derivative forms when any acetylene containing compound is photolysed in presence of ironpentacarbonyl in hexane solution [5,58]. ORTEP diagram of compounds **7** and **8** are shown in Figs. 5 and 6 respectively.

Table 1
Crystal data and structure refinement parameters for compounds **2**, **3**, **4**, **5**, **7** and **8**.

Compound	**2**	3.CH_2Cl_2	**4**	5.CH_2Cl_2	**7**	**8**
Empirical formula	$C_{18}H_{10}FeO_4$	$C_{37}H_{20}Cl_2Fe_2O_8$	$C_{35}H_{20}Fe_2O_7$	$C_{36}H_{22}Cl_2Fe_2O_7$	$C_{22}H_{14}Fe_2O_4$	$C_{25}H_{14}Fe_2O_7$
Formula wt.	346.11	775.13	664.21	749.14	454.03	538.06
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic
Spacegroup	P 2_1/c	P 2_1/c	P 2_1 2_1 2_1	P-1	P-1	P 2_1/n
a, Å	6.5965(2)	9.2635(6)	8.2853(2)	11.5919(10)	6.3970(2)	9.1172(3)
b, Å	12.3155(3)	14.6879(9)	16.2348(5)	11.7133(14)	6.8058(4)	24.5770(6)
c, Å	18.3500(5)	25.803(2)	21.1882(6)	12.6860(16)	20.5310(8)	9.6731(2)
α, deg	90	90	90	105.575(11)	91.002(4)	90
β, deg	94.747(2)	92.373(6)	90	90.579(9)	95.004(3)	96.344(2)
γ, deg	90	90	90	99.400(9)	93.280(4)	90
Volume, Å^3	1485.63(7)	3507.8(4)	2850.03(14)	1634.3(3)	888.76(7)	2168.39(10)
Z	4	4	4	2	2	4
D_{calcd}, Mg/m^3	1.547	1.468	1.548	1.522	1.697	1.648
Abs coeff, mm^{-1}	1.032	1.030	1.070	1.100	1.659	1.384
F(000)	704	1568	1352	760	460	1088
Crystal size, mm	0.28 × 0.23 × 0.18	0.33 × 0.28 × 0.23	0.33 × 0.28 × 0.23	0.23 × 0.18 × 0.13	0.33 × 0.29 × 0.26	0.31 × 0.28 × 0.23
θ range, deg	3.31 to 25.00	3.45 to 25.00	3.36 to 25.00	3.34 to 25.00	3.27 to 25.00	3.27 to 25.00
Index ranges	−7<=*h*<=7, −14<=*k*<=14, −21<=*n*<=21	−11<=*h*<=10, −17<=*k*<=17, −30<=*l*<=29	−9<=*h*<=9, −19<=*k*<=19, −24<=*l*<=25	−13<=*h*<=13, −13<=*k*<=13, −15<=*l*<=10	−7<=*h*<=6, −7<=*k*<=8, −23<=*l*<=24	−9<=*h*<=10, −28<=*k*<=29, −11<=*l*<=11
Reflections collected/unique	10626/2611 [R(int) = 0.0198]	28184/6155 [R(int) = 0.0527]	23481/5003 [R(int) = 0.0634]	11279/5612 [R(int) = 0.0527]	6143/3129 [R(int) = 0.0271]	17199/3810 [R(int) = 0.0514]
Completeness to $\theta = 25$	99.8%	99.7%	99.6%	97.7%	99.8%	99.8%
Data/restraints/parameters	2611/0/208	6155/0/442	5003/0/397	5612/0/424	3129/0/253	3810/0/307
Goodness-of-fit on F^2	1.063	1.071	0.982	0.852	1.100	0.966
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0243$, wR2 = 0.0674	$R1 = 0.0748$, wR2 = 0.2267	$R1 = 0.0349$, wR2 = 0.0790	$R1 = 0.0633$, wR2 = 0.1551	$R1 = 0.0719$, wR2 = 0.2162	$R1 = 0.0335$, wR2 = 0.0664
R indices (all data)	$R1 = 0.0305$, wR2 = 0.0687	$R1 = 0.1033$, wR2 = 0.2386	$R1 = 0.0427$, wR2 = 0.0807	$R1 = 0.1320$, wR2 = 0.1727	$R1 = 0.0770$, wR2 = 0.2196	$R1 = 0.0535$, wR2 = 0.0697
Largest diff. peak and hole	0.241 and −0.152 e.A^{-3}	0.737 and −0.446 e.A^{-3}	0.599 and −0.229 e.A^{-3}	0.683 and −0.693 e.A^{-3}	2.902 and −0.632e.A^{-3}	0.409 and −0.277 e.A^{-3}

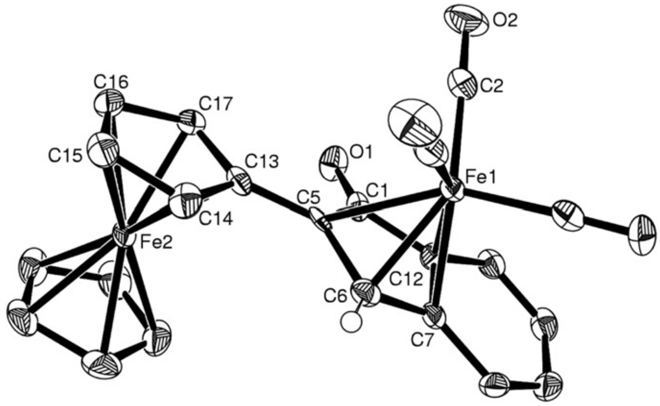


Fig. 5. ORTEP diagram of compound 7 with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Fe1—C6 = 2.049(5), Fe1—C7 = 2.121(5), Fe1—C5 = 2.147(4), Fe1—C12 = 2.178(5), Fe1—C1 = 2.399(5), C1—C12 = 1.471(7), C1—C5 = 1.490(6), C5—C6 = 1.443(7), C6—C7 = 1.417(7), C7—C12 = 1.435(7), C7—C8 = 1.437(7), C8—C9 = 1.364(7), C9—C10 = 1.432(7), C10—C11 = 1.341(7), C11—C12 = 1.433(7); C4—Fe1—C2 = 97.7(2), C4—Fe1—C3 = 91.6(2), C2—Fe1—C3 = 102.0(2), O2—C2—Fe1 = 178.4(5), O3—C3—Fe1 = 178.1(5), O4—C4—Fe1 = 178.9(5), C12—C1—C5 = 104.1(4), C6—C5—C1 = 107.8(4), C7—C6—C5 = 108.9(4), C6—C7—C12 = 108.2(4), C7—C12—C1 = 108.8(4).

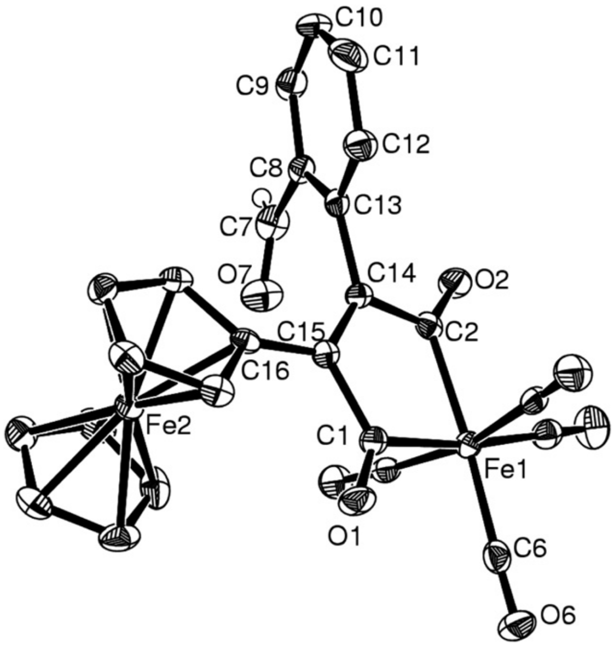


Fig. 6. ORTEP diagram of compound 8 with 50% probability ellipsoids: Selected bond lengths (Å) and bond angles (deg): Fe1—C1 = 2.015(3), Fe1—C2 = 2.015(3), C1—C15 = 1.511(4), C2—C14 = 1.506(4), C14—C15 = 1.336(4), C1—Fe1—C2 = 82.31(11), C15—C1—Fe1 = 113.4(2), C14—C15—C1 = 114.8(2), C15—C14—C2 = 116.8(2), C14—C2—Fe1 = 112.43(19), O3—C3—Fe1 = 175.2(3), O4—C4—Fe1 = 178.3(3), O5—C5—Fe1 = 177.1(3), O6—C6—Fe1 = 177.4(3).

The yield of tricarbonyl(2-ferrocenylindenone)iron **7** (22%) is much higher than its phenyl analogue (9%). Possibly the steric crowding due to ferrocene prevents two molecules to come together and hence prevent the formation of ferracyclopentadiene ring, as we have observed in the case of phenyl substituted products. Thus ferrocenyl substituted reactant prefers intramolecular C—C bond formation while in phenyl substituted reactant intermolecular C—C bond formation competes with the intramolecular C—C bond formation.

At room temperature, stirring of compounds **2** and **7** in dichloromethane in presence of diiodine (1 h) results in quantitative formation of the previously reported indenone compound **9** [59] and new ferrocenyl derivative, **10** respectively (Scheme 4). The demetallated product was confirmed by IR and ^{1}H NMR spectroscopy. The IR spectra of these compounds (**9** and **10**) show absence of metal carbonyl peaks as well as large shift in cyclic ν(CO).

3. Conclusion

In conclusion, we have demonstrated a one step photochemical synthesis of phenyl and ferrocenyl substituted tricarbonylironindenone complexes and their clean conversion to respective indenones. We have seen that ferrocenyl substituted ortho ethynylbenzaldehyde gives higher yield of indenoneironcarbonyl compared to phenyl substituted one. In case of phenyl substituted ortho ethynylbenzaldehyde intermolecular coupling is preferred over intramolecular coupling.

4. Experimental

4.1. General procedures

All reactions and manipulations were performed using standard Schlenk line techniques under an inert atmosphere of pre-purified nitrogen or argon. Solvents were purified, dried and distilled under argon or nitrogen atmosphere prior to use. Infrared spectra were recorded on Nicolet 380 FTIR spectrometer. NMR spectra were recorded on Varian VXR-300S and Bruker AVANCE^{III}/400 spectrometer with TMS as internal standard. Ferrocenylacetylene was prepared by established procedure [60]. Iron pentacarbonyl, phenyl acetylene and 2-bromobenzaldehyde were purchased from Fluka, Aldrich and Spectrochem, respectively, and were used without further purification. Photochemical reactions were carried out in a water cooled double-walled quartz vessel having a 125 W mercury lamp manufactured by SAIC. TLC plates were purchased from Merck (20 × 20 cm, silica gel 60 F254). 2-(phenylethynyl) benzaldehyde and 2-(ferrocenylethynyl)benzaldehyde were prepared by cuprous iodide free Sonogashira coupling [61,62].

4.2. Crystal structure determination

Suitable X-ray quality crystals of compounds **2** to **5**, **7** and **8** were grown by slow evaporation of n-hexane and dichloromethane solution at 0 °C–5 °C, and X-ray crystallographic data were collected. Oxford Diffraction X caliber-S, CCD system equipped with area detector was used for the cell determination and intensity data collection for compounds. Monochromatic Mo $K\alpha$ radiation (0.71359 Å) was used for the measurements. Absorption corrections using multi ψ-scans were applied. Structures were solved by direct methods (SHELXS) and refined by full-matrix least squares against F_o^2 using SHELXL-97 software [63]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. The crystal and refinement data are summarized in Table 1.

4.3. General procedure for photolysis of ironpentacarbonyl and 2-(phenylethynyl)benzaldehyde and 2-(ferrocenylethynyl) benzaldehyde

4.3.1. Photolysis of 2-(phenylethynyl)benzaldehyde with Fe(CO)$_5$

To a solution of 2-(phenylethynyl)benzaldehyde (410 mg, 2.04 mmol), in dry hexane (60 mL), Fe(CO)$_5$ (0.4 mL, 2.92 mmol) was added and the mixture was photolysed at 0 °C for 30 min. The solvent was removed under reduced pressure, and the residue was subjected to a chromatographic workup on silica gel TLC plates using dichloromethane/hexane solvent mixtures as eluent, which afforded 105 mg of unreacted 2-(phenylethynyl)benzaldehyde along with compound **2** (45 mg, 9%), **3** (97 mg, 20%), **4** (74 mg, 16%), **5** (52 mg, 11%).

4.3.2. Photolysis of 2-(ferrocenylethynyl)benzaldehyde with $Fe(CO)_5$

To a solution of 2-(ferrocenylethynyl)benzaldehyde (240 mg, 0.76 mmol), in dry hexane (60 mL), $Fe(CO)_5$ (0.2 mL, 1.46 mmol) was added and the mixture was photolysed at 0 °C for 30 min. The solvent was removed under reduced pressure, and the residue was subjected to a chromatographic workup on silica gel TLC plates by using dichloromethane/hexane solvent mixtures as eluent, which afforded 38 mg of unreacted 2-(ferrocenylethynyl)benzaldehyde along with compound **7**(62 mg, 22%) and **8**(24 mg, 7%).

4.3.3. General procedure for demetallation of 2-(phenylethynyl) benzaldehyde and 2-(ferrocenylethynyl)benzaldehyde

0.1 mmol of compound was taken in 20 mL dichloromethane. To this solution 0.2 mmol of diiodine was introduced and stirred for 60 min. Reaction mixture was worked up using sodium thiosulphate solution in water to remove excess diiodine. Product was collected in dichloromethane, dried over sodium sulphate. The solvent was removed under reduced pressure. (Yield of **9** is 19 mg, 91% and yield of **10** is 29 mg, 94%.)

5. Analytical data

Compound **2**:Orange solid; IR (νC = O in hexane, cm^{-1}) 2050 (s), 1992 (m), 1974 (s), 1625 (s); ^1H NMR (δ in ppm, $CDCl_3$): 6.52, 7.22 to 8.01; ^{13}C NMR (δ in ppm, $CDCl_3$): 67.5 (CH-Cph), 91.2 (CPh), 102.7(C=C–C=O), 123.0 to 132.5 (aromatic carbons), 167.2 (cyclic C=O), 209.4(Fe–CO); % C = 62.94, % H = 3.01.

Compound **3**: Maroon solid; IR (νC = O in hexane, cm^{-1}): 2069 (s), 2023 (s), 1997 (s), 1911 (m), 1689 (s); ^1H NMR (δ in ppm, $CDCl_3$): 7.0–8.0 (m, aromatic), 10.0 (CHO); ^{13}C NMR (δ in ppm, $CDCl_3$): 68.3, 71.9, 127.8–136.4 (aromatic), 193.4 (PhCHO), 215.2 (Fe–CO); % C = 62.90, % H = 2.93.

Compound **4**: Maroon solid; IR (νC = O in hexane, cm^{-1}): 2048, 1982, 1913, 1729, 1697; ^1H NMR (δ in ppm, $CDCl_3$): 6.6–7.9 (m, aromatic), 8.9 (HCO–Fe), 10.2 (CHO); ^{13}C NMR (δ in ppm, $CDCl_3$): 68.3 and 71.9 (C=C), 125.4–136.0 (aromatic), 190.9 (PhCHO), 199.5 (HCO–Fe), 205.8 to 220.3 (Fe–CO); % C = 63.51, % H = 3.62.

Compound **5**: Maroon solid; IR (νC = O in hexane, cm^{-1}): 2050, 1986, 1927, 1720 1691; ^1H NMR (δ in ppm, $CDCl_3$): 6.7–7.7 (aromatic), 8.9 (HCO–Fe), 9.9 (CHO); ^{13}C NMR (δ in ppm, $CDCl_3$): 68.3 and 71.9 (C=C), 126.3–136.9 (aromatic), 190.5 (PhCHO), 199.7 (HCO–Fe), 206.2 to 219.9 (Fe–CO); % C = 58.21, % H = 3.11.

Compound **7**: Maroon solid; IR (νC = O in KBr, cm^{-1}): 2051, 1994, 1978, 1629; ^1H NMR (δ in ppm, $CDCl_3$): 4.0–4.3 (m, 9H, C_5H_5 and C_5H_4), 5.9 (CH = Cfc), 7.1–7.7 (m, 4H, aromatic); ^{13}C NMR (δ in ppm, $CDCl_3$): 67.4 (CH = Cfc), 68.8–70.4 (C_5H_5 and C_5H_4), 90.6 (CH = Cfc), 101.4(C=C–C=O), 123.2 to 131.9 (aromatic), 166.3 (cyclic CO), 209.7 (Fe–CO); % C = 58.38, % H = 3.59.

Compound **8**: Blue solid; IR (νC = O in hexane, cm^{-1}): 2113 (s), 2065 (s), 2042 (s), 2023 (s), 1699 (s), 1648 cm^{-1}(s); ^1H NMR (δ in ppm, $CDCl_3$): 4.1–4.8 (m, 9H, C_5H_5 and C_5H_4), 6.9–8.0 (m, 4H, aromatic), 9.9 (CHO); ^{13}C NMR (δ in ppm, $CDCl_3$): 69–73.5 (ferrocene), 129.2–136.7 (aromatic), 165.5 (=Cfc) 169 (=CPh), 191.44 (–CHO), 199.2, 199.3 (cyclic CO), 202.3, 202.9 (Fe–CO); % C = 62.01, % H = 3.78.

Compound **9**: Orange solid; IR (νC = O in KBr, cm^{-1}): 1725 (s); ^1H NMR (δ in ppm, $CDCl_3$): 7.1–7.56 (m, 8H, aromatic), 7.59 (s, 1H, C=CH), 7.88 (d, 1H, o-H to C=O); ^{13}C NMR (δ in ppm, $CDCl_3$): 121.17–136.19 (aromatic), 143.35(C=CPh), 144.95(C=CPh), 198.81(CO); m+1/z = 207.14; % C = 88.09, % H = 5.21.

Compound **10**: Green solid; IR (νC = O in KBr, cm^{-1}): 1712 (s); ^1H NMR (δ in ppm, $CDCl_3$): 4.1–4.8 (m, 9H, C_5H_5 and C_5H_4), 6.9–7.5 (m, 3H, aromatic), 7.6(s, 1H, C=CH), 7.81(d, 1H, o-H to C=O); ^{13}C NMR (δ, $CDCl_3$): 67.7–77.5(C_5H_5 and C_5H_4), 121–137.7 (6C, aromatic carbon), 138.2 (C=CFc), 145.5(C=CFc), 196.7 (CO); m+1/z = 315.06; % C = 72.11, % H = 4.78.

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Appendix A. Supplementary material

CCDC 825969(**2**), 825970(**3**), 825971(**4**), 825972(**5**), 825968(**7**), and 825973(**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre. CCDC nos. 825969, 825970, 825971, 825972, 825968, and 825973 for compounds **2**, **3**, **4**, **5**, **7** and **8** respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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