

## Thermal and Photochemical Reactions of $\eta^5$ -Cyclopentadienyl(naphthoyl)-(dicarbonyl)iron Complexes with Alkynes: Formation of Benzindenones and Dihydropentalenones

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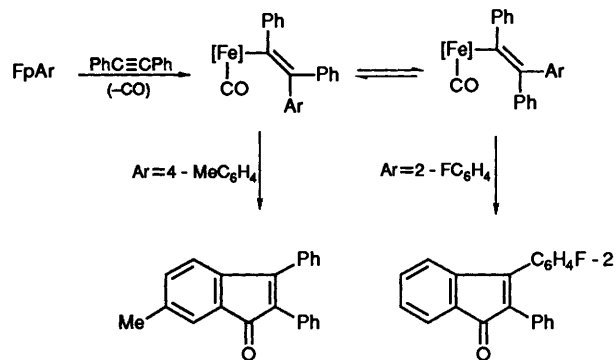
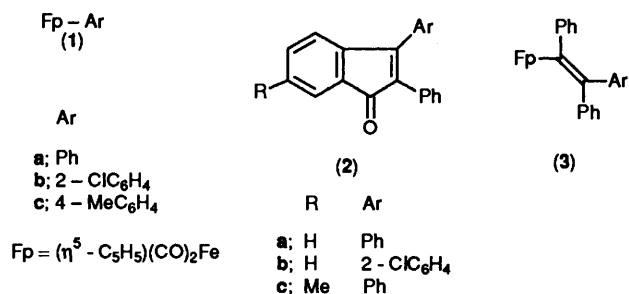
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$\eta^5$ -Cyclopentadienyl(1- and 2-naphthoyl)(dicarbonyl)iron complexes (**6a**) and (**6b**) have been synthesised from the appropriate acid chlorides and sodium  $\eta^5$ -cyclopentadienyl(dicarbonyl)iron(1-). UV irradiation of (**6a**) and (**6b**) separately with diphenylacetylene in benzene gives 1,2-diphenyl-3*H*-benz[*e*]inden-3-one (**8**), and 2,3-diphenyl-1*H*-benz[*e*]inden-1-one (**7**) respectively, together with smaller quantities of bis( $\eta^5$ -cyclopentadienyl)(tetracarbonyl)di-iron. The benz[*e*]indenones (**7**) and (**8**) are also formed in low yield from diphenylacetylene and  $\eta^5$ -cyclopentadienyl(1- and 2-naphthoyl)(dicarbonyl)iron complexes respectively, in hot decalin. A second product from the thermal reaction is *c*-4,*c*-6*a*-dihydro-4-(1- or 2-naphthyl)-2,3-diphenylpentalen-1(*r*-3*aH*)-one (**9a**) or (**9b**), respectively, incorporating a cyclopentadienyl group. A compound of the last type (**9c**) is also formed in a thermal reaction of  $\eta^5$ -cyclopentadienyl(1-naphthoyl)(dicarbonyl)iron with 1-phenylpropyne. The molecular structures of (**7**) and (**9a**) were elucidated by X-ray crystallography.

We have recently shown that aryl complexes of  $\eta^5$ -cyclopentadienyl(dicarbonyl)iron, (Fp), of type (**1**) react thermally with diphenylacetylene to give indenone products in reasonable yields [*e.g.* (**1a**, **b**)  $\rightarrow$  (**2a**, **b**); (**1c**)  $\rightarrow$  (**2c**)].<sup>1</sup> We have



Scheme 1.

subsequently shown<sup>2</sup> that thermolyses of alkenyl iron complexes (**3**) also produce indenones [*cf.* (**2**)] in improved yields. This evidence lends weight to our original suggestion<sup>1</sup> that such alkenyl complexes, formed by insertion of acetylene into the Fe-aryl bond, are intermediates in the synthesis of indenones from FpAr (Scheme 1).

Indenones and their heterocyclic analogues have also been prepared by UV irradiation of mixtures of diphenylacetylene and aryl complexes Fp(COAr) [Ar = Ph, 2-thienyl, 2-(5-methylfuryl), 2-benzofuryl].<sup>3</sup> Reactions of the heterocyclic aryl complexes are reported to be regioselective, giving only one indenone analogue assigned structure (**4**) with the CO function *ortho* to the original heteroatom.<sup>3,4</sup>

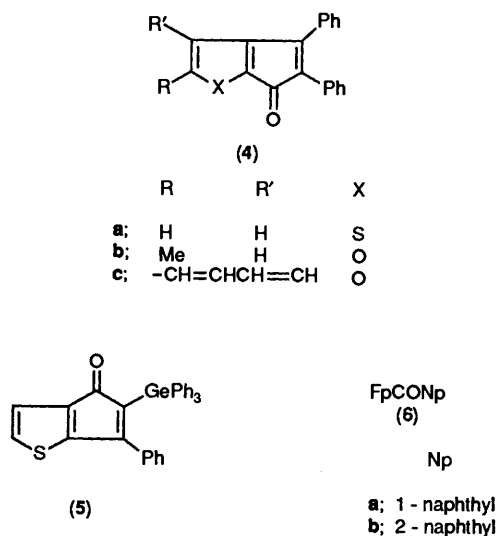
It is known<sup>5</sup> that photochemical decarbonylation of complexes FpCOAr occurs, and it is to be expected that the resulting Fp-Ar intermediate would react by a similar mechanism to that of preformed Fp-Ar; if product formation involves an intermediate of type (**3**) then the regioselectively formed indenone analogue would have structure of type (**5**), contrary to that reported. Moreover, it is notable that the reaction of Fp(CO-2-

thienyl) with Ph<sub>3</sub>GeC≡CPh affords a single condensed thiophene derivative of structure (**5**) and this product, unlike the other related compounds, has been definitively structurally characterized by X-ray diffraction.<sup>6</sup> This result is in accord with our proposed mechanism and does not require the postulated, unusual rearrangement of a spirocyclic intermediate.<sup>6</sup>

In the present study we have evaluated the regiochemical outcome of formation of benz[*e*]indenones from both thermal and photochemical reactions of naphthoyl complexes (**6a**) and (**6b**) with acetylene derivatives, and contrast the organic product distribution under the two conditions. Further mechanistic conclusions on indenone formation have been drawn. Also, unusual co-products containing the dihydropentalen-1-one system are formed by incorporation of a cyclopentadienyl group.

### Results and Discussion

1-Naphthoyl (**6a**) and 2-naphthoyl (**6b**) complexes were prepared routinely from the appropriate naphthoyl chlorides and sodium  $\eta^5$ -cyclopentadienyl(dicarbonyl)ferrate. UV irradiation



of the complexes (**6a**, **b**) separately under nitrogen with an equimolar quantity of diphenylacetylene in benzene caused complete decomposition of the complexes as noted from the disappearance of the acyl (C=O) bands in the IR spectra at 1606 and 1611  $\text{cm}^{-1}$ , respectively. The solutions were left to stand exposed to air for 2 days and then chromatographed. The product from complex (**6b**) afforded unchanged diphenylacetylene (33%), bis-( $\eta^5$ -cyclopentadienyl)(tetracarbonyl)di-iron ( $\text{Fp}_2$ ) (27%) and a compound (21%) assumed to be a benzindenone derivative. The m.p. (167–169 °C) of this crimson compound was close to that (167–168 °C) of the product formed from the reaction of phenylmagnesium bromide and 2-phenyl-2,3-dihydrobenz[e]indene-1,3-dione and assigned<sup>7</sup> as 2,3-diphenyl-1*H*-benz[e]inden-1-one (**7**). Since structural differentiation of benzindenone regioisomers by conventional spectroscopic methods (IR, UV, NMR) is unreliable, an X-ray crystallographic analysis of a single crystal of the compound isolated above was undertaken.

The solid-state molecular structure, as determined by X-ray crystallography, is depicted in Figure 1, and is clearly consistent with structural formula (**7**). The refined bond distances and angles, and the fractional atomic co-ordinates are listed in Tables 1 and 2, respectively.

The crystal structure consists of well separated molecules of (**7**) with no intermolecular contacts significantly shorter than the sum of the respective van der Waal's radii between pairs of non-hydrogen atoms. There is generally good agreement between corresponding bond lengths and angles around the benzindenone ring system in both (**7**) and the 2,3-dichloro-2,6,8-tri-*t*-butyl derivative.<sup>8</sup> As in the latter compound, the ring atoms are co-planar within  $\pm 0.06$  Å and the enone double bond is found to be essentially localised [C(2)–C(3) 1.351 (3) Å]. The phenyl groups at C(2) and C(3) are rotated out of co-planarity with the benzindenone ring plane by 37 and 53° respectively, an arrangement which closely resembles that adopted by the phenyl substituents in 6-methyl-2,3-diphenylindenone.<sup>1</sup>

By a similar work-up procedure, complex (**6a**) gave unchanged diphenylacetylene (33%),  $\text{Fp}_2$  (27%) and an isomeric compound assigned the structure 1,2-diphenyl-3*H*-benz[e]inden-3-one (**8**) (30%). The latter was identical (mixed m.p., TLC, IR) to the compound prepared in this work from 2-naphthoyl chloride, diphenylacetylene, and aluminium trichloride<sup>9</sup> and also identical with a product obtained by us in a trace amount by heating 2-naphthaldehyde and diphenylacetylene in di-*t*-butyl peroxide.<sup>10</sup>

Thermal reactions of complexes (**6a**) and (**6b**) with acetylene

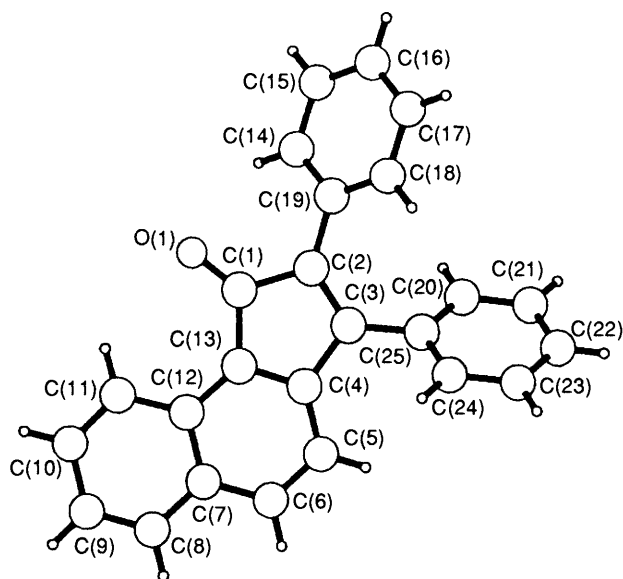


Figure 1. The molecular structure of the benzindenone derivative (**7**) (PLUTO<sup>33</sup>).

derivatives in hot decalin gave complex products with only moderate to poor yields of isolable compounds. For example, the 1-naphthoyl complex (**6a**) and diphenylacetylene gave the expected benz[e]indenone derivative (**8**) (27%) and trace amounts of 1-naphthylferrocene and bis-1,1'-(1-naphthyl)ferrocene. In addition, a colourless solid with the molecular formula  $\text{C}_{30}\text{H}_{22}\text{O}$  was formed (24%); this suggested that the 1-naphthoyl moiety had combined with one diphenylacetylene and one cyclopentadienyl fragment but the structure could not be unambiguously assigned from <sup>1</sup>H NMR and IR data. X-Ray crystallographic analysis indicated that the compound was one of the possible diastereoisomers of a trisubstituted 4,6a-dihydropentalen-1(3*aH*)-one (**9a**).

The crystal structure consists of well separated molecules of compound (**9a**). The structure of a single molecule of (**9a**) is illustrated in Figure 2 together with the numbering system

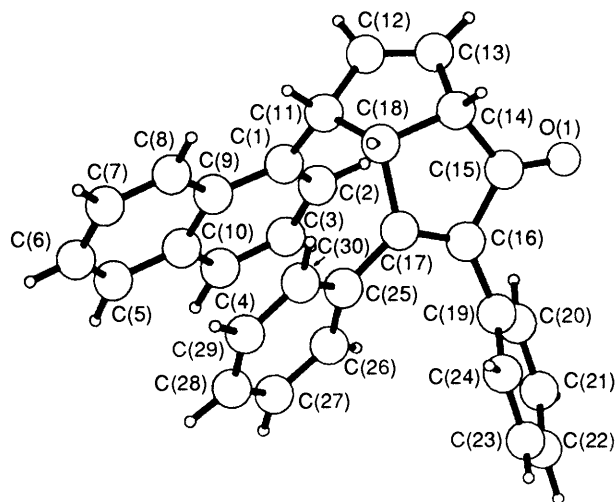


Figure 2. The molecular structure of the pentalenone derivative (**9a**) (PLUTO<sup>33</sup>).

adopted. The pentalenone ring system of (**9a**) has a *cis*-fused ring junction [torsion angle: H(14)–C(14)–C(18)–H(18) 3.15°] which has been observed previously for related pentalen-

**Table 1.** Derived geometrical parameters for benzindenone derivative (7).

(a) Bond lengths (Å) with estimated standard deviations			
O(1)–C(1)	1.214(3)	C(5)–C(6)	1.371(4)
C(1)–C(2)	1.516(3)	C(6)–C(7)	1.414(4)
C(1)–C(13)	1.484(3)	C(7)–C(8)	1.407(4)
C(2)–C(3)	1.351(3)	C(7)–C(12)	1.431(3)
C(2)–C(19)	1.487(3)	C(8)–C(9)	1.364(4)
C(3)–C(4)	1.495(3)	C(9)–C(10)	1.397(4)
C(3)–C(25)	1.480(3)	C(10)–C(11)	1.360(4)
C(4)–C(5)	1.397(3)	C(11)–C(12)	1.419(4)
C(4)–C(13)	1.378(3)	C(12)–C(13)	1.408(3)
(b) Angles (°) with estimated standard deviations			
O(1)–C(1)–C(2)	126.15(22)	C(6)–C(7)–C(8)	121.32(23)
O(1)–C(1)–C(13)	127.39(22)	C(6)–C(7)–C(12)	119.50(22)
C(2)–C(1)–C(13)	106.45(19)	C(8)–C(7)–C(12)	119.17(22)
C(1)–C(2)–C(3)	107.54(20)	C(7)–C(8)–C(9)	120.9(3)
C(1)–C(2)–C(19)	122.24(18)	C(8)–C(9)–C(10)	120.1(3)
C(3)–C(2)–C(19)	130.15(20)	C(9)–C(10)–C(11)	121.1(3)
C(2)–C(3)–C(4)	109.28(20)	C(10)–C(11)–C(12)	120.54(25)
C(2)–C(3)–C(25)	129.13(20)	C(7)–C(12)–C(11)	118.13(22)
C(4)–C(3)–C(25)	121.60(19)	C(7)–C(12)–C(13)	116.81(21)
C(3)–C(4)–C(5)	129.35(21)	C(11)–C(12)–C(13)	125.06(22)
C(3)–C(4)–C(13)	109.55(20)	C(1)–C(13)–C(4)	107.10(20)
C(5)–C(4)–C(13)	121.00(21)	C(1)–C(13)–C(12)	130.76(21)
C(4)–C(5)–C(6)	118.58(23)	C(4)–C(13)–C(12)	122.10(21)
C(5)–C(6)–C(7)	121.97(23)		

**Table 2.** Fractional co-ordinates of atoms with e.s.d.'s for the benzindenone derivative (7).

	x	y	z
O(1)	–0.057 91(20)	0.054 51(22)	0.376 15(9)
C(1)	0.049 5(3)	0.070 58(24)	0.338 33(12)
C(2)	0.041 7(3)	0.057 17(23)	0.264 62(11)
C(3)	0.182 9(3)	0.091 67(23)	0.240 58(11)
C(4)	0.291 0(3)	0.121 85(23)	0.296 01(11)
C(5)	0.450 4(3)	0.150 9(3)	0.294 76(12)
C(6)	0.526 7(3)	0.169 3(3)	0.352 94(12)
C(7)	0.448 7(3)	0.160 86(24)	0.413 65(12)
C(8)	0.528 1(3)	0.182 1(3)	0.472 94(13)
C(9)	0.452 5(3)	0.171 2(3)	0.531 33(13)
C(10)	0.294 2(4)	0.138 1(3)	0.532 86(13)
C(11)	0.212 2(3)	0.117 4(3)	0.476 83(13)
C(12)	0.286 2(3)	0.128 41(24)	0.415 07(12)
C(13)	0.212 1(3)	0.109 70(23)	0.354 32(11)
C(14)	–0.202 46(18)	–0.079 76(16)	0.256 71(7)
C(15)	–0.336 80(18)	–0.119 25(16)	0.223 31(7)
C(16)	–0.372 86(18)	–0.059 99(16)	0.163 20(7)
C(17)	–0.274 59(18)	0.038 75(16)	0.136 47(7)
C(18)	–0.140 25(18)	0.078 25(16)	0.169 87(7)
C(19)	–0.104 19(18)	0.018 99(16)	0.229 98(7)
C(20)	0.209 59(19)	–0.007 33(13)	0.128 70(7)
C(21)	0.261 94(19)	0.001 51(13)	0.064 32(7)
C(22)	0.339 18(19)	0.118 64(13)	0.042 98(7)
C(23)	0.364 08(19)	0.226 93(13)	0.086 02(7)
C(24)	0.311 74(19)	0.218 09(13)	0.150 41(7)
C(25)	0.234 49(19)	0.100 96(13)	0.171 75(7)

ones.<sup>11,12</sup> *cis*-Fused bicyclo[3.3.0] hydrocarbons are predicted to be inherently less strained than the corresponding *trans*-fused isomers.<sup>13</sup> The carbon atoms within each of the five-membered rings are found to be co-planar within  $\pm 0.04$  Å and the calculated dihedral angle between the planes is 121.6°.

Consistent with the mechanism proposed for the formation of (9a) (*vide infra*), the 1-naphthyl substituent at C(11) is located on the concave face of the molecule. To minimise intramolecular

**Table 3.** Derived geometrical parameters for pentalenone derivative (9a).

Bond lengths (Å) and angles (°) involving non-H atoms			
O–C(15)	1.215 8(24)	C(14)–C(18)	1.536(3)
C(1)–C(2)	1.374(3)	C(15)–C(16)	1.470 3(25)
C(1)–C(9)	1.433 5(25)	C(16)–C(17)	1.348(3)
C(1)–C(11)	1.516 5(25)	C(16)–C(19)	1.477(3)
C(2)–C(3)	1.402(3)	C(17)–C(18)	1.511 2(25)
C(3)–C(4)	1.359(3)	C(17)–C(25)	1.447 3(24)
C(4)–C(10)	1.412(3)	C(19)–C(20)	1.382(3)
C(5)–C(6)	1.353(3)	C(19)–C(24)	1.393(3)
C(5)–C(10)	1.415(3)	C(20)–C(21)	1.387(3)
C(6)–C(7)	1.393(4)	C(21)–C(22)	1.367(4)
C(7)–C(8)	1.364(3)	C(22)–C(23)	1.366(4)
C(8)–C(9)	1.418(3)	C(23)–C(24)	1.385(3)
C(9)–C(10)	1.424(3)	C(25)–C(26)	1.388(3)
C(11)–C(12)	1.504(3)	C(25)–C(30)	1.387(3)
C(11)–C(18)	1.586(3)	C(26)–C(27)	1.376(3)
C(12)–C(13)	1.311(3)	C(27)–C(28)	1.360(5)
C(13)–C(14)	1.489(3)	C(28)–C(29)	1.368(5)
C(14)–C(15)	1.522(3)	C(29)–C(30)	1.383(4)
C(2)–C(1)–C(9)	118.65(16)	C(14)–C(15)–C(16)	108.17(16)
C(2)–C(1)–C(11)	119.07(16)	C(15)–C(16)–C(17)	109.47(16)
C(9)–C(1)–C(11)	122.24(16)	C(15)–C(16)–C(19)	123.64(16)
C(1)–C(2)–C(3)	122.18(19)	C(17)–C(16)–C(19)	126.89(15)
C(2)–C(3)–C(4)	119.80(20)	C(16)–C(17)–C(18)	112.88(15)
C(3)–C(4)–C(10)	121.03(19)	C(16)–C(17)–C(25)	126.97(16)
C(6)–C(5)–C(10)	120.85(21)	C(18)–C(17)–C(25)	120.11(16)
C(5)–C(6)–C(7)	120.42(21)	C(11)–C(18)–C(14)	106.16(15)
C(6)–C(7)–C(8)	120.43(22)	C(11)–C(18)–C(17)	115.45(15)
C(7)–C(8)–C(9)	121.54(21)	C(14)–C(18)–C(17)	104.06(15)
C(1)–C(9)–C(8)	123.79(17)	C(16)–C(19)–C(20)	120.26(17)
C(1)–C(9)–C(10)	119.00(16)	C(16)–C(19)–C(24)	121.61(19)
C(8)–C(9)–C(10)	117.20(17)	C(20)–C(19)–C(24)	118.04(19)
C(4)–C(10)–C(5)	121.23(19)	C(19)–C(20)–C(21)	121.06(21)
C(4)–C(10)–C(9)	119.25(17)	C(20)–C(21)–C(22)	120.01(25)
C(5)–C(10)–C(9)	119.51(18)	C(21)–C(22)–C(23)	119.88(23)
C(1)–C(11)–C(12)	113.05(16)	C(22)–C(23)–C(24)	120.66(23)
C(1)–C(11)–C(18)	115.61(14)	C(19)–C(24)–C(23)	120.26(24)
C(12)–C(11)–C(18)	102.07(15)	C(17)–C(25)–C(26)	121.35(17)
C(11)–C(12)–C(13)	114.14(19)	C(17)–C(25)–C(30)	120.02(18)
C(12)–C(13)–C(14)	112.49(18)	C(26)–C(25)–C(30)	118.55(18)
C(13)–C(14)–C(15)	114.05(17)	C(25)–C(26)–C(27)	120.82(23)
C(13)–C(14)–C(18)	104.96(17)	C(26)–C(27)–C(28)	120.0(3)
C(15)–C(14)–C(18)	105.03(15)	C(27)–C(28)–C(29)	120.24(24)
O–C(15)–C(14)	125.30(17)	C(28)–C(29)–C(30)	120.5(3)
O–C(15)–C(16)	126.52(18)	C(25)–C(30)–C(29)	119.8(3)

steric interactions, the 1-naphthyl and phenyl groups at C(11) and C(17) adopt a spatial arrangement such that the angle between their respective ring planes is relatively small (13.8°). In general, the geometrical parameters around the molecule are in good agreement with the expected values.<sup>14</sup> The derived bond distances and angles, and the final refined atomic co-ordinates for the non-hydrogen atoms are listed in Tables 3 and 4 respectively.

The 2-naphthyl complex (6b) reacted thermally with diphenylacetylene in similar fashion to give 2,3-diphenyl-1H-benz[e]inden-1-one (7) (32%), hexaphenylbenzene (5%), and a trace of a component believed to contain bis-1,1'-(2-naphthyl)ferrocene and unchanged diphenylacetylene (TLC, <sup>1</sup>H NMR); also isolated (7%) was an analytically pure sample of the 2-naphthyl analogue (9b) of the pentalenone derivative described above (9a). A product of the latter type (9) was also isolated (16%) from the complex product resulting from the reaction of complex (6a) with 1-phenylpropyne. The structure of this single isomer is tentatively assigned as (9c) from comparison of its <sup>1</sup>H NMR spectrum with that of (9a). Thus a diminution of resonances occurs in the highfield portion of the

**Table 4.** Atomic parameters  $x$ ,  $y$ ,  $z$  and for the pentalenone derivative (**9a**).

	$x$	$y$	$z$
O	0.484 02(10)	0.286 50(20)	0.543 56(8)
C(1)	0.648 47(11)	0.105 35(20)	0.303 43(10)
C(2)	0.591 63(12)	-0.002 87(22)	0.329 03(13)
C(3)	0.546 62(14)	-0.109 69(24)	0.275 11(13)
C(4)	0.557 67(14)	-0.106 48(25)	0.194 41(13)
C(5)	0.628 41(15)	0.003 1(3)	0.080 25(13)
C(6)	0.686 28(16)	0.103 3(3)	0.052 04(14)
C(7)	0.735 05(16)	0.205 8(3)	0.105 34(13)
C(8)	0.723 66(13)	0.208 40(24)	0.186 31(12)
C(9)	0.663 89(11)	0.106 10(20)	0.219 17(11)
C(10)	0.616 27(12)	-0.000 06(21)	0.164 13(11)
C(11)	0.689 75(12)	0.223 35(22)	0.364 17(11)
C(12)	0.718 90(13)	0.160 0(3)	0.448 42(12)
C(13)	0.681 13(13)	0.226 88(25)	0.506 75(13)
C(14)	0.616 15(14)	0.348 41(24)	0.474 86(11)
C(15)	0.516 08(13)	0.312 04(22)	0.480 49(11)
C(16)	0.465 82(12)	0.315 02(19)	0.397 14(10)
C(17)	0.524 99(12)	0.340 85(19)	0.342 65(10)
C(18)	0.623 05(13)	0.356 16(23)	0.382 61(11)
C(19)	0.365 98(12)	0.290 38(22)	0.378 72(10)
C(20)	0.327 20(14)	0.157 9(3)	0.402 31(12)
C(21)	0.235 24(15)	0.126 1(3)	0.378 51(14)
C(22)	0.181 13(16)	0.227 7(3)	0.332 00(15)
C(23)	0.217 25(16)	0.361 9(3)	0.310 66(15)
C(24)	0.309 02(16)	0.394 7(3)	0.333 82(13)
C(25)	0.503 18(12)	0.349 18(21)	0.252 51(10)
C(26)	0.440 68(14)	0.251 1(3)	0.209 72(12)
C(27)	0.424 90(17)	0.254 1(3)	0.125 42(13)
C(28)	0.470 73(22)	0.354 0(4)	0.082 95(16)
C(29)	0.531 96(22)	0.453 0(4)	0.123 78(17)
C(30)	0.548 96(16)	0.451 3(3)	0.208 47(14)

aromatic region of (**9c**) which suggests that the methyl substituent is remote from the carbonyl group. It is possible that the other regioisomer (**9d**) is formed, but cannot be isolated from the complex reaction mixture containing 1-naphthylferrocene, bis-1,1'-(1-naphthyl)ferrocene, and  $\eta^5$ -cyclopentadienyl(1-naphthyl)dicarbonyliron.

The structures of the benz[*e*]indenones produced either photochemically or thermally in this work are consistent with a mechanism of formation which involves preliminary deinsertion of CO from the naphthoyl complexes (**6a**) or (**6b**) followed by insertion of diphenylacetylene into the resulting Fe-Np bond. Cyclisation to form a benz[*e*]indenone from an intact naphthoyl ligand, as suggested by Russian workers for related aryl systems,<sup>3,4</sup> would not produce a benz[*e*]indenone of the correct structure.

The overall mechanism may involve the steps shown in Scheme 2. We have identified Fp-Np (**10**) as a by-product (step i). Acetylene complexes of type (**11**), although not isolated from these reactions, are found in related photochemical reactions of Fp(C<sub>6</sub>H<sub>4</sub>X-2) (X = F, Cl)<sup>15</sup> and are related to [Fe(SnPh<sub>3</sub>)(CO)(PhC<sub>2</sub>Ph)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)].<sup>16</sup> The photochemically induced insertion of an acetylene into Fe-alkyl bonds is recorded<sup>17</sup> (*cf.* step iii); generally, acetylene insertions into M-C bonds may give *Z*- or *E*-products<sup>17,18</sup> and isomerisations between these forms have been observed. For the iron derivatives [Fe(alkenyl)(CO)L( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] isomerisation of the alkenyl ligand is oxidatively catalysed.<sup>19</sup> Also, CO insertion into Fe-alkenyl bonds (*cf.* step v) occurs readily in the presence of oxidative catalysts.<sup>20</sup> In the formation of benz[*e*]indenones only the *Z*-form of the alkenyl ligand is involved in the subsequent cyclisation *via ortho*-metallation. The order of *ortho*-metallation (step vi or vii) relative to carbonyl insertion (steps v or viii or ix) is not clear but the overall sequences of Scheme 2 followed by reductive

elimination will produce the observed benz[*e*]indenone. It may be noted that for the 2-naphthoyl derivative (**6b**), metallation and cyclisation occur only at the 1- and not the 3-position, in accord with the site of greater reactivity for electrophilic substitution.

The production of trisubstituted 4,6a-dihydropentalen-1(3a*H*)-ones of depicted stereochemistry (**9**) must involve migration of a naphthyl group to a co-ordinated cyclopentadienyl ring. It may be noted that transfer of aryl groups occurs within complexes [Co(COAr)(PMe<sub>3</sub>)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)]<sup>+</sup> to give ring substituted products [Co(CO)(PMe<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Ar)] in the presence of bases,<sup>21</sup> and related base-induced migrations from iron to the cyclopentadienyl ring of silyl and other ligands are reported.<sup>22</sup> A possible mechanism for the formation of compounds (**9**) is given in Scheme 3 but more studies are required to establish the detailed sequence of reactions.

### Experimental

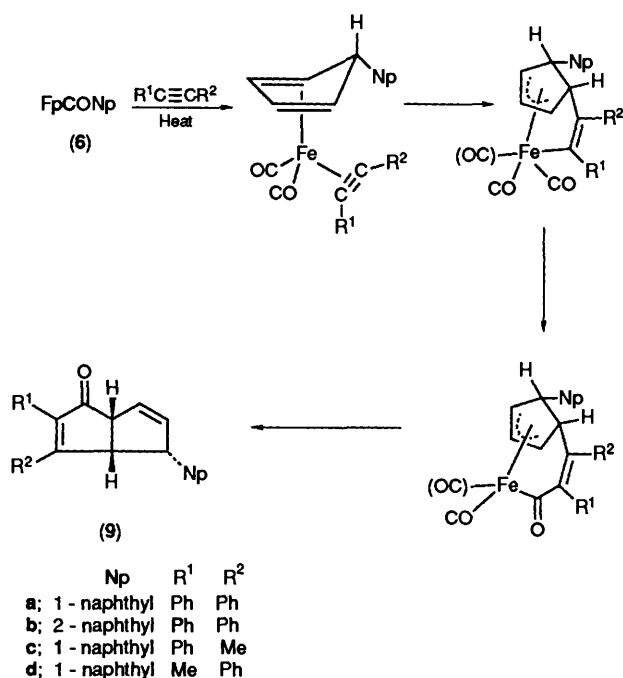
IR spectra were recorded on a Perkin-Elmer 580 instrument calibrated against polystyrene. <sup>1</sup>H NMR spectra were recorded at 200 or 300 MHz on Bruker WP200 SY or Varian XL-300 instruments respectively with SiMe<sub>4</sub> as reference. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk techniques. Solvents used were dried under reflux and freshly distilled from the agents shown in parentheses: benzene and xylenes (Na), dichloromethane (P<sub>2</sub>O<sub>5</sub>), tetrahydrofuran (Na/benzophenone) and chloroform (P<sub>2</sub>O<sub>5</sub>).

1-Naphthoyl chloride [m.p. 50.5–52 °C (lit.,<sup>23</sup> 51–52 °C)] and 2-naphthoyl chloride [b.p. 114 °C/0.25 Torr (lit.,<sup>24</sup> 163 °C/10 Torr)] were prepared in 69 and 91% yields, respectively, from naphthoic acids and phosphorus pentachloride as described in ref. 23. Mass spectra were recorded on a VG-100 Analytical instrument at 70 MeV using thermal ionisation.

*Preparation of  $\eta^5$ -Cyclopentadienyl(1-naphthoyl)(dicarbonyl)iron (6a).*—Sodium  $\eta^5$ -cyclopentadienyl(dicarbonyl)iron(1-) (18.5 mmol) was prepared<sup>5</sup> from  $\eta^5$ -cyclopentadienyl(dicarbonyl)iron dimer (3.27 g, 9.25 mmol) with 4% sodium amalgam in tetrahydrofuran (40 ml) at room temperature. The solution was cooled to -78 °C and added to a stirred solution of 1-naphthoyl chloride (3.53 g, 18.5 mmol) in tetrahydrofuran at -78 °C. After 2 h, the mixture was allowed to stand at room temperature for 48 h. The product was evaporated to dryness under reduced pressure and extracted with chloroform (7 × 10 ml). The chloroform extract was evaporated under reduced pressure and the residue was extracted with light petroleum (10 × 20 ml) to afford  $\eta^5$ -cyclopentadienyl(1-naphthoyl)(dicarbonyl)iron (**6a**) (2.28 g, 37%), m.p. 103.5–106.5 °C;  $\nu_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>) 2 024, 1 968 (Fe-CO), and 1 606 cm<sup>-1</sup> (aroyl CO);  $\delta$ (CDCl<sub>3</sub>) 4.94 (s, 5 H  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) and 7.23–7.93 (m, 7 H, Ar-H); *m/z* 304 [*M*<sup>+</sup> - CO], 277 (10), 276 (51; *M*<sup>+</sup> - 2CO), 249 (19), 248 (100; *M*<sup>+</sup> - 3CO) 247 (15), 246 (79), 244 (8), 272 (8), 192 (21), 191 (37), 190 (74), and 189 (16) (Found: C, 65.2; H, 3.8. C<sub>18</sub>H<sub>12</sub>FeO<sub>3</sub> requires C, 65.1; H, 3.6%).

*Preparation of  $\eta^5$ -Cyclopentadienyl(2-naphthoyl)(dicarbonyl)iron (6b).*—This compound was prepared as described above to give crude material (42%), m.p. 78–82 °C (decomp.). Column chromatography (active neutral alumina) with light petroleum-dichloromethane as eluant gave analytically pure, golden yellow/brown  $\eta^5$ -cyclopentadienyl(2-naphthoyl)(dicarbonyl)iron (**6b**), m.p. 101–102 °C;  $\nu_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>) 2 027, 1 969 (Fe-CO), and 1 611 cm<sup>-1</sup> (aroyl CO);  $\delta$ (CDCl<sub>3</sub>) 4.95 (s, 5 H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) and 7.0–8.5 (m, 7 H, Ar-H); *m/z* 304 (20%; *M*<sup>+</sup> - CO), 277 (11), 276 (53); *M*<sup>+</sup> - 2CO), 249 (19), 248 (100; *M*<sup>+</sup> - 3CO), 247 (16), 246 (79), 244 (8), 222 (9), 192 (22), 191 (36), 190 (79), and 189





Scheme 3.

crystal and molecular structure determination of compound (7) is described later.

**Reactions of 1-Naphthoyl Chloride and 2-Naphthoyl Chloride with Diphenylacetylene and Aluminium Trichloride.**—A mixture of the either 1- or 2-naphthoyl chloride (2.90 g, 10 mmol) and anhydrous aluminium trichloride (1.34 g, 10 mmol) in dichloromethane (25 ml) were stirred at  $-10^{\circ}\text{C}$  for 45 min. After being allowed to warm to room temperature, the mixture was stirred for a further 2 h. It was then hydrolysed with 6M HCl, the dichloromethane layer was separated and combined with further dichloromethane extracts ( $2 \times 20$  ml) of the aqueous layer. After being dried over  $\text{MgSO}_4$ , the filtered solution was evaporated under reduced pressure until precipitation had just begun. The materials were chromatographed (neutral alumina) with diethyl ether–dichloromethane (90:10) eluant to afford the red products 2,3-diphenyl-1*H*-benz[*e*]inden-1-one (7) (43%) or 1,2-diphenyl-3*H*-benz[*e*]inden-3-one (8) (40%) respectively. They were recrystallised from dichloromethane–hexane to give deep red/violet crystalline materials with physical and spectral parameters identical with those described above.

**Thermal Reaction of  $\eta^5$ -Cyclopentadienyl(1-naphthoyl)(dicarbonyl)iron (6a) with Diphenylacetylene.**— $\eta^5$ -Cyclopentadienyl(1-naphthoyl)(dicarbonyl)iron (1.0 g, 3.3 mmol) and diphenylacetylene (1.10 g, 6.2 mmol) were heated under reflux in decalin (35 ml) for 10 min. The product was cooled and eluted through a column of neutral alumina prepared using hexane. Elution with hexane removed the decalin and unchanged diphenylacetylene (0.15 g); hexane–diethyl ether (90:10) gave trace amounts of 1-naphthylferrocene and bis-1,1'-naphthylferrocene which were identical (m.p., IR, NMR) with authentic samples.<sup>25</sup> Continued elution with hexane–diethyl ether (1:1) gave a pale orange fraction from which *c*-4,*c*-6a-dihydro-4-(1-naphthyl)-2,3-diphenylpentalen-1(*r*-3aH)-one (9a) (0.29 g, 24%) was obtained as colourless crystals;  $\delta(\text{CDCl}_3)$  3.98 (m, 1 H), 4.70 (dd, 1 H), 5.14 (m, 1 H), 5.81 (m, 1 H), 6.26–6.46 (m, 5 H), 6.94 (m, 2 H), 7.03 (d, 1 H), 7.14–7.24 (m, 7 H), 7.36 (d, 1 H), 7.41 (d, 1 H), and 7.81 (d, 1 H);  $m/z$  398 (100%;  $M^{+}$ ), 397 (5), 371 (6), 370 (17), 369 (5), 354 (4), 291 (12), 279 (11), 278 (9), 277 (5), 276 (5),

246 (12), 239 (4), 233 (35), 215 (14), 191 (13), 189 (10), 178 (11), 167 (16), 166 (74), 165 (34), and 152 (17) (Found: C, 90.55; H, 5.6.  $\text{C}_{30}\text{H}_{22}\text{O}$  requires C, 90.4; H, 5.6%). The crystal and molecular structure determination of this compound is described below. Further elution with diethyl ether gave a deep red fraction containing 1,2-diphenyl-3*H*-benz[*e*]inden-3-one (8) (0.27 g, 27%), followed by  $\text{Fp}_2$  (0.11 g, 21%), and finally a deep violet fraction of tetraphenylcyclopentadienone (112 mg), identical ( $^1\text{H}$  NMR) with an authentic sample. A deep orange residue remained on the column. Concentration of supernatant solutions yielded hexaphenylbenzene (*ca.* 80 mg).

**Thermal Reaction of  $\eta^5$ -Cyclopentadienyl(2-naphthoyl)(dicarbonyl)iron (6b) with Diphenylacetylene.**— $\eta^5$ -Cyclopentadienyl(2-naphthoyl)(dicarbonyl)iron and diphenylacetylene were allowed to react as described above, and the product was chromatographed [silica gel, diethyl ether–light petroleum (1:9) eluant]. The following were isolated: unchanged diphenylacetylene (43%), hexaphenylbenzene (5%), a trace component believed to be bis-1,1'-(2-naphthyl)ferrocene and 2,3-diphenyl-1*H*-benz[*e*]inden-1-one (7) (32%); the latter was identical (m.p., IR,  $^1\text{H}$  NMR) to the compound described earlier. Further elution with diethyl ether–light petroleum (1:4) gave *c*-4,*c*-6a-dihydro-4-(2-naphthyl)-2,3-diphenylpentalen-1(*r*-3aH)-one (9b) (7%), m.p. 236–238  $^{\circ}\text{C}$ ;  $\delta(\text{CDCl}_3)$  3.98 (m, 1 H), 4.72 (dd, 1 H), 5.16 (m, 1 H), 5.83 (m, 1 H), 6.24–6.55 (m, 5 H), 6.85–7.50 (m, 12 H), and 7.82 (d, 1 H);  $m/z$  398 (100%;  $M^{+}$ ) 399 (32), 370 (18), 291 (13), 279 (11), 233 (24), 215 (21), 203 (14), 202 (19), 189 (26), 178 (34), 166 (57), 165 (68), and 152 (34) (Found: C, 90.5; H, 5.4.  $\text{C}_{30}\text{H}_{22}\text{O}$  requires C, 90.4; H, 5.6%).

**Thermal Reaction of  $\eta^5$ -Cyclopentadienyl(2-naphthoyl)(dicarbonyl)iron (6b) with 1-phenylpropyne.**— $\eta^5$ -Cyclopentadienyl(1-naphthoyl)(dicarbonyl)iron (1.0 g, 3.3 mmol) and 1-phenylpropyne (1.0 g, 8.6 mmol) were heated under reflux in xylenes (isomer mixture) (20 ml) for 1 h. The product was chromatographed as described in the preceding experiment to give the following fractions (eluting solvents indicated in parentheses): (a) (hexane): trace amounts of 1-naphthylferrocene and bis-1,1'-(1-naphthyl)ferrocene; (b) [hexane–diethyl ether (3:7)]:  $\eta^5$ -cyclopentadienyl(1-naphthyl)(dicarbonyl)iron (0.14 g, 15%) identified spectroscopically, *e.g.*  $\delta(\text{CDCl}_3)$  4.95 (s, 5 H) and 7.10–8.10 (m, 7 H, Ar-H);  $m/z$  304 (20%;  $M^{+}$ ), 277 (11), 276 (53;  $M^{+} - \text{CO}$ ), 249 (19), 248 (100;  $M^{+} - 2\text{CO}$ ), 247 (16), and 246 and (80); *c*-4,*c*-6a-dihydro-3-methyl-4-(1-naphthyl)-2-phenylpentalen-1(*r*-3aH)-one (9c) (0.16 g, 16%);  $\delta(\text{CDCl}_3)$  0.83 (s, 3 H), 3.97 (m, 1 H), 3.98 (ddd, 1 H), 5.25 (br d, 1 H), 5.78 (d, 1 H), 6.15 (ddd, 1 H), 6.99 (d, 2 H), 7.01–7.65 (m's, 7 H), 7.82 (d, 1 H), 7.88 (d, 1 H), and 8.30 (d, 1 H);  $m/z$  336 (63%;  $M^{+}$ ), 321 (15), 293 (10), 292 (5), 291 (7), 289 (6), 279 (4), 278 (8), 229 (7), 226 (6), 215 (15), 191 (7), 171 (18), 167 (18), 166 (100), 165 (30), 155 (11), 153 (12), 152 (32), and 149 (22) (Found: C, 89.6; H, 6.2.  $\text{C}_{25}\text{H}_{20}\text{O}$  requires C, 89.3; H, 6.0%);  $\text{Fp}_2$  trace; and  $\eta^5$ -cyclopentadienyl(1-naphthoyl)(dicarbonyl)iron (0.12 g, 12%) identical (m.p.; IR) with an authentic sample.

**X-Ray Structure Determination of Benzindenone Derivative (7).**—*Crystal data.*  $\text{C}_{25}\text{H}_{16}\text{O}$ ,  $M = 332.4$ , dark red prisms, monoclinic, space group  $P2_1/n$  (non-standard setting of No. 14),  $a = 8.5842(11)$ ,  $b = 9.7915(21)$ ,  $c = 20.466(4)$  Å,  $\beta = 90.015(15)^{\circ}$ ,  $Z = 4$ ,  $D_c = 1.283$  g cm $^{-3}$ ,  $F(000) = 696$ ,  $\mu\text{-Mo-K}\alpha = 0.72$  cm $^{-1}$ , crystal dimensions *ca.* 0.45  $\times$  0.375  $\times$  0.225 nm.

**Data Collection and Reduction.**—The intensity data were collected over the quadrant ( $h$ ,  $-10$  to  $+10$ ,  $k$ ,  $0$  to  $+11$ ,  $l$ ,  $0$  to  $+24$ ;  $1.5 < \theta < 25^{\circ}$ ) on a CAD-4 diffractometer using  $\omega$ - $2\theta$  scanning and graphite monochromated Mo- $K\alpha$  X-radiation ( $\lambda = 0.710693$  Å). 1 853 Out of 3 031 unique data measured had

$I > 3\sigma(I)$  and were used in subsequent structure solution and refinement. The intensity data were corrected for Lorentz and polarisation effects, but not for absorption.

**Structure Solution and Refinement.**—The positions of the non-hydrogen atoms were readily located by application of 'direct methods' (SHELXS86<sup>26</sup>). The hydrogen atoms were subsequently located on a series of difference Fourier maps and included in the refinement process at calculated positions (C–H 0.95 Å) and with a fixed isotropic temperature factor ( $U_{\text{iso}} = 0.08 \text{ \AA}^2$ ). The phenyl substituents were treated as rigid hexagons (C–C 1.395 Å). Full matrix least-squares refinement of the structure (SHELX76<sup>27</sup>) using anisotropic temperature factors for the non-hydrogen atoms reduced the discrepancy factors  $R$  and  $R_w$  to 0.046 and 0.067 respectively at convergence. The weighting scheme  $w^{-1} = [\sigma^2(F) + 0.00262(F^2)]$  gave satisfactory analyses of variance. The final difference Fourier map contained no features greater than  $\pm 0.22 \text{ e}^- \text{ \AA}^{-3}$ , with a general noise level of  $ca. \pm 0.12 \text{ e}^- \text{ \AA}^{-3}$ . Incidental crystallographic calculations were carried out using the program CALC.<sup>28</sup>

**X-Ray Structure Determination of Pentalenone Derivative (9a).**—Crystal data.  $\text{C}_{30}\text{H}_{22}\text{O}$ ,  $M = 398.5$ , colourless needles, monoclinic, space group  $P2_1/n$  (non-standard setting of No. 14),  $a = 14.7140(9)$ ,  $b = 8.8538(8)$ ,  $c = 16.4499(4)$  Å,  $\beta = 97.525(4)^\circ$ ,  $Z = 4$ ,  $D_c = 1.246 \text{ g cm}^{-3}$ ,  $F(000) = 840$ ,  $\mu(\text{Mo-K}\alpha) = 0.70 \text{ cm}^{-1}$ , crystal dimensions  $ca. 0.2 \times 0.2 \times 0.35 \text{ mm}$ .

**Data Collection and Reduction.**—The intensity data were collected over the quadrant ( $h, -17$  to  $+17$ ,  $k, 0$  to  $+10$ ,  $l, 0$  to  $+19$ ;  $1.5 < \theta < 25^\circ$ ) on a CAD-4 diffractometer driven by the NRCCAD software package<sup>29</sup> using  $\omega$ - $2\theta$  scanning and graphite monochromated Mo- $K\alpha$  X-radiation ( $\lambda = 0.710693$  Å). Of 3735 unique data measured, 2465 had  $I > 2.5\sigma(I)$  and were used in subsequent structure solution and refinement. The intensity data were corrected for Lorentz and polarisation effects, but not for absorption.

**Structure Solution and Refinement.**—The positions of the non-hydrogen atoms were readily located by application of 'direct methods' (MULTAN<sup>30</sup>). The hydrogen atoms were subsequently located on a series of difference Fourier maps. Full matrix least-squares refinement of the structure (NRCVAX<sup>31</sup>) using anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms reduced the discrepancy factors  $R$  and  $R_w$  to 0.037 and 0.039 respectively at convergence. The weighting scheme  $w^{-1} = [\sigma^2(F) + 0.00025(F^2)]$  gave satisfactory analyses of variance. The final difference Fourier map, which contained no chemically significant features, had a general background level less than  $\pm 0.14 \text{ e}^- \text{ \AA}^{-3}$ .

The atomic scattering factors were taken from 'International Tables for X-ray Crystallography'<sup>32</sup>. Tables of anisotropic thermal parameters and fractional co-ordinates for hydrogen atoms for the crystal structures of (7) and (9a) are available from the Cambridge Crystallographic Data Centre.\*

\* For details, see 'Instructions for Authors (1990)', *J. Chem. Soc., Perkin Trans. 1*, 1990, Issue 1.

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