Hydrocarbon Complexes of Iron, Ruthenium, and Osmium. Part X.[1] Carbonyl-iron and -ruthenium Complexes Derived from 6-(*trans*-Prop-1-enyl)fulvene

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6-(*trans*-Prop-1-enyl)fulvene reacts with [$Fe_2(CO)_9$] or [$Ru_3(CO)_{12}$] to give complexes of composition [$M_2(CO)_5$-(C_9H_{10})] (M = Fe or Ru) in which the organic ligand is η^5-cyclopentadienyl-bonded to one metal atom and η^3-allyl-bonded to the other. An additional product of the enneacarbonyldi-iron reaction is a complex [$Fe_2(CO)_6$-(C_9H_{12})] in which the propenyl substituent has become saturated, while the reaction between dodecacarbonyltriruthenium and 6-(*trans*-prop-1-enyl)fulvene also produces [$Ru_2(CO)_4(C_{18}H_{20})$], a complex containing two linked molecules of the fulvene.

RECENT studies have shown that several carbonylruthenium complexes effect dehydrogenative transannular cyclisation of cyclo-octatetraenes and cyclo-octatrienes forming complexes of the unstable hydrocarbon pentalene (1) and its derivatives.[2] In an extension of this work we have investigated the reactions of [$Ru_3(CO)_{12}$] and [$Fe_2(CO)_9$] with 6-(*trans*-prop-1-enyl)fulvene (2).[3] This hydrocarbon has been shown[4] to cyclise upon vapour-phase pyrolysis, yielding the substituted dihydropentalene (3) and several of its bond-shift isomers; moreover, dihydropentalenes are known sources of pentalene complexes upon reaction with iron carbonyls.[5] In view of the established ability of both [$Ru_3(CO)_{12}$] and [$Fe_2(CO)_9$] to induce both ring closure

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[1] Part IX, S. A. R. Knox, R. P. Phillips, and F. G. A. Stone, *J.C.S. Dalton*, 1976, 552.

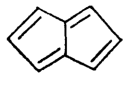
[2] S. A. R. Knox and F. G. A. Stone, *Accounts Chem. Res.*, 1974, **7**, 321.

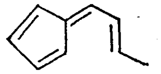
[3] M. Neuenschwander, D. Meuche, and H. Schaltegger, *Helv. Chim. Acta*, 1964, **47**, 1022.

[4] J. J. Gajewski and C. J. Cavender, *Tetrahedron Letters*, 1971, 1057.

[5] D. F. Hunt and J. W. Russell, *J. Amer. Chem. Soc.*, 1972, **94**, 7198; *J. Organometallic Chem.*, 1976, **104**, 373.

and hydrogen abstraction with hydrocarbons it seemed possible, therefore, that reaction of compound (2) with the carbonyls might provide a direct and convenient route to pentalene complexes.


(1)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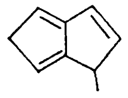
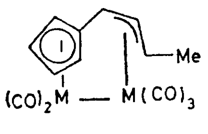

(3)

RESULTS AND DISCUSSION

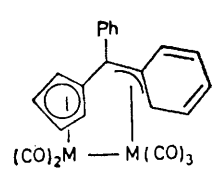
The possibility expressed above was not realised in practice, although several complexes of interest were identified from reactions of compound (2) with [$Ru_3(CO)_{12}$] or [$Fe_2(CO)_9$]. In neither case was the desired ring closure achieved. On stirring compound (2) with [$Fe_2(CO)_9$] in hexane for 2 days two products were obtained. Analytical and mass spectroscopic data indicated the formulation [$Fe_2(CO)_5(C_9H_{10})$] for the air-stable red crystalline major product (30% yield), to which structure (4; M = Fe) is assigned on the basis of ^1H and ^{13}C n.m.r. spectra. Thus, in the ^1H spectrum signals at τ 4.77 (1 H, d), 5.10 (2 H, m), and 5.25 (1 H, m) are in the region typical of η-cyclopentadienyl ring protons, while signals at τ 6.19 (1 H, br, s), 7.07 (1 H, br, s), and 7.89 (1 H, m) are attributed to three allylic protons. The methyl group appears as a doublet at τ 8.57 (3 H). Consistent with this proposal, the ^{13}C n.m.r. spectrum has signals corresponding to the methyl carbon at 20.08, to the allylic carbons at 50.54, 63.04, and 71.71, and to the ring carbons at 80.27, 82.27, 87.12, and 90.58 p.p.m., downfield of tetramethylsilane. A very weak signal at 85 p.p.m. can be assigned to the carbon of the ring which does not bear a proton.

Structure (4) shows the cyclopentadienyl ring *anti* and the methyl group *syn* with respect to the central proton of the allyl group. There are reasonable grounds for the assumption of this methyl group position, for it maintains the original *trans*-olefin geometry. The *anti*-orientation of the cyclopentadienyl substituent seems more likely than the *syn*-alternative, which demands an intuitively unlikely structure. Striking support for structure (4) comes from very recent studies [6] of the reactions of 6,6-diphenylfulvene with iron and ruthenium carbonyls. Complexes [$M_2(CO)_5(C_5H_4CPh_2)$] (M = Fe or Ru) were obtained and shown by *X*-ray diffraction to have structure (5), closely related to (4), in which an allyl group has been formed *via* the destruction of the aromatic character of a phenyl ring. Note that in these molecules the cyclopentadienyl ring is also in an *anti*-orientation. Both compounds (4) and (5) are probably formed from complexes of type (6) which are known [7,8] products of the reactions of several fulvenes with iron carbonyls. In the cases under attention here, unsaturation in the groups R^1 or R^2 of (6) allows release of a molecule of carbon monoxide and ready formation of an η^3-allyl grouping. Complex (4; M = Fe) is very stable relative to a species of the form (6), since even under extreme conditions no uptake of carbon monoxide by (4) was observed.

The minor product (10%) of the reaction of ennea-carbonyldi-iron with (2) was a red oil for which analytical and mass spectroscopic data indicated the formulation [$Fe_2(CO)_6(C_9H_{12})$], *i.e.* addition of two atoms of hydrogen to the fulvene had occurred. Apart from resonances due to aliphatic protons (partially obscured by hydrocarbon impurities), the ^1H n.m.r. spectrum of the red oil showed three signals at τ 5.03 (2 H, m), 5.83 (1 H, m), and 6.13 (1 H, m). If these are attributed to η-cyclopentadienyl ring protons the most likely structure for this complex becomes (6; M = Fe, R^1 = H, R^2 = Pr^n) in which the propenyl substituent of the fulvene has become saturated.



(4) M = Fe,Ru



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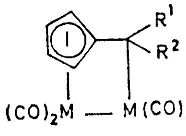
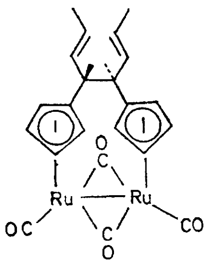
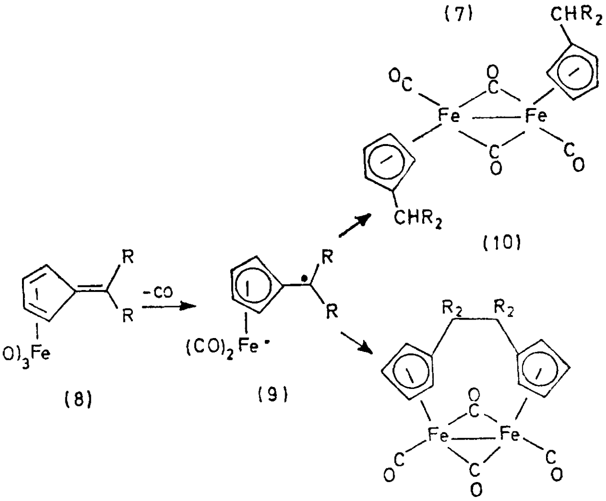


(6) M = Fe, Ru



(7)



(11)

The reaction of compound (2) with [$Ru_3(CO)_{12}$]

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[6] U. Behrens and E. Weiss, *J. Organometallic Chem.*, 1975, **96**, 399, 435.

[7] R. C. Kerber and D. J. Ehntholt, *Synthesis*, 1970, 449.

[8] E. Weiss and W. Hübel, *Chem. Ber.*, 1962, **95**, 1186.

proceeds readily in heptane at reflux giving a yellow crystalline complex $[Ru_2(CO)_5(C_9H_{10})]$. Mass, i.r., and ^{1}H n.m.r. spectra clearly establish that this species is the ruthenium analogue (4; M = Ru) of the previously discussed iron compound. In the same reaction an orange crystalline complex was formed in similar yield (*ca.* 30%), a product without parallel in the iron carbonyl reaction. A molecular ion in the mass spectrum at *m/e* 551 with a distinct Ru_2 isotope pattern, and other ions indicating the loss of four carbonyl groups, corresponded to a molecular formulation $[Ru_2(CO)_4(C_{18}H_{20})]$. In addition, an absorption due to bridging carbonyl groups was observed in the i.r. region, while the ^{1}H n.m.r. spectrum had an array of signals between τ 4.2 and 5.4 (total relative intensity 12 H) and others at τ 7.8 (1 H, m), 8.3 (1 H, m), and 9.0 (6 H, m). These data fit well a structure *e.g.* (7), analogues of which are known [8] as products of the reactions of some fulvenes with iron carbonyls. The low-field group of n.m.r. signals are assigned to the combined η-cyclopentadienyl and free olefinic protons, with the remaining resonances attributed to *trans* protons attached to the carbons linking the fulvenes (τ 7.8, 8.3) and to the methyl groups (τ 9.0). The simplicity of the i.r. spectrum of (7) (ν_{CO} 2 007s, 1 952w, and 1 829m cm^{-1}) is conducive with little or no population of a non-carbonyl-bridged isomer.

The formation of iron analogues of (7) has been explained [6] as arising *via* the transient complex $[Fe(CO)_3$-(fulvene)] [*e.g.* (8)] which ejects carbon monoxide to yield the diradical (9). Dimerisation then proceeds either with hydrogen abstraction, yielding (10), or with coupling of the two hydrocarbon groups to give (11). The size of R appears to exert a controlling influence on the choice of dimerisation route, in that small substituents R favour (11) while large R groups lead to (10). This same control is evidently exerted with carbonylruthenium complexes also, for though (7) is obtained from (2), the reaction of pentamethylenefulvene with $[Ru_3(CO)_{12}]$ led to a complex of type (10).[6]

EXPERIMENTAL

I.r. and ^{1}H n.m.r. spectra were recorded using Perkin-Elmer 257 and Varian Associates HA 100 instruments, respectively. A JEOL PFT-100 spectrometer operating in the Fourier-transform mode at 25.15 MHz was used to obtain ^{13}C n.m.r. spectra, with $CDCl_3$ as internal reference. Mass spectra were obtained using an AEI MS902 instrument operating at 70 eV ionising potential.* Hydrocarbon solvents were dried by distillation from calcium hydride, and all reactions were performed under a nitrogen atmosphere. 6-(*trans*-Prop-1-enyl)fulvene (2) was prepared by a literature method.[3]

Reaction of 6-(trans-*Prop*-1-*enyl)fulvene* (2) *with* $[Fe_2(CO)_9]$.—Enneacarbonyldi-iron (4.6 g, 12.6 mmol) and compound (2) (0.12 g, 1.0 mmol) were stirred in hexane (100 cm^3) for 41 h. After removal of solvent and $[Fe(CO)_5]$ at reduced pressure, the residue was extracted with hexane and the concentrated extract introduced into a short alumina column. Elution with hexane developed two red bands, the first giving (46 mg, 9%) a red *oil*, purified by distillation (50 °C/10^{-2} Torr), identified as $[Fe_2(CO)_6(C_9H_{12})]$ (6; M = Fe, R^1 = H, R^2 = Pr^n) (Found: C, 45.1; H, 2.8%; *M*, 400. $C_{15}H_{12}O_6Fe_2$ requires C, 45.0; H, 3.0%; *M*, 400), $\nu_{max.}$(CO) 2 075m, 2 008sh, 1 998s, 1 977w, and 1 946w cm^{-1} (hexane solution). The ^{1}H n.m.r. spectrum ($CDCl_3$ solution) showed resonances at τ 5.03 (2 H, m), 5.83 (1 H, m), 6.13 (1 H, m), and 7.48 (1 H, m) in addition to unresolved aliphatic proton signals between τ 8 and 9, partially obscured by hydrocarbon impurities. The second red band was removed with dichloromethane–hexane (1 : 9) and yielded (0.1 g, 32%) red *crystals* of $[Fe_2(CO)_5(C_9H_{10})]$ (4; M = Fe) (Found: C, 45.6; H, 2.8%; *M*, 370. $C_{14}H_{10}O_5Fe_2$ requires C, 45.4; H, 2.7%; *M*, 370), m.p. 136—137 °C; $\nu_{max.}$(CO) 2 043m, 1 988s, 1 971m, and 1 944w cm^{-1} (hexane solution). The ^{1}H n.m.r. spectrum ($CDCl_3$ solution) had signals at τ 4.77 (1 H, d, *J* 6 Hz), 5.10 (2 H, m), 5.25 (1 H, m), 6.19 (1 H, br, s), 7.07 (1 H, br, s), 7.89 (1 H, m), and 8.57 (3 H, d, *J* 6 Hz), while the ^{13}C n.m.r. spectrum had signals at 20.08, 50.54, 63.04, 71.71, 80.27, 82.27, 85.0, 87.12, and 90.58 p.p.m. (downfield of $SiMe_4$).

Reaction of 6-(trans-*Prop*-1-*enyl)fulvene* (2) *with* $[Ru_3(CO)_{12}]$.—A heptane (100 cm^3) solution of compound (2) (0.9 g, 8.0 mmol) and $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) was heated at reflux for 12 h; the solvent was then removed and the residue extracted with hexane. Chromatography on a 50-cm alumina column with hexane as eluant afforded a trace of an unidentified complex and then (105 mg, 29%) yellow *crystals* of $[Ru_2(CO)_5(C_9H_{10})]$ (4; M = Ru) (Found: C, 35.6; H, 2.2%; *M*, 461. $C_{14}H_{10}O_5Ru_2$ requires C, 36.4; H, 2.2%; *M*, 461), m.p. 136 °C, $\nu_{max.}$(CO) 2 060m, 2 005s, 1 990s, and 1 945m cm^{-1} (hexane solution). The ^{1}H n.m.r. spectrum ($CDCl_3$ solution) had signals at τ 4.52 (1 H, m), 4.86 (3 H, m), 6.30 (1 H, m), 6.74 (1 H, m), 7.62 (1 H, m), and 8.54 (3 H, d, *J* 6 Hz). Further elution with dichloromethane–hexane (1 : 1) gave (135 mg, 31%) orange *crystals* of $[Ru_2(CO)_4(C_{18}H_{20})]$ (7) (Found: C, 46.1; H, 3.7; *M*, 551. $C_{22}H_{20}O_4Ru_2$ requires C, 47.9; H, 3.6%; *M*, 551), m.p. 175—176 °C, $\nu_{max.}$(CO) 2 007s, 1 952w, and 1 829m cm^{-1} (hexane solution). The ^{1}H n.m.r. spectrum ($CDCl_3$ solution) had signals at τ 4.2—5.4 (12 H, m), 7.8 (1 H, m), 8.3 (1 H, m), and 9.0 (6 H, m).

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* eV ≈ 1.60×10^{-19} J.