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Preliminary communication

ANNELATION OF RING-OPENED CYCLOPROPENIUM IONS TO COORDINATED CYCLOOCTATETRAENE, AND THE X-RAY STRUCTURE OF $[Fe(CO)_3\{\sigma,\eta^3\text{-}C_8H_9(C_3Ph_3)\}]$

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Summary

The X-ray structure of $[Fe(CO)_3\{\sigma,\eta^3\text{-}C_8H_9(C_3Ph_3)\}]$, prepared by hydride ion addition to the product of the reaction between $[Fe(CO)_3(\eta^4\text{-COT})]$ (COT = cyclooctatetraene) and $[C_3Ph_3]^+$, reveals annelation of the ring-opened cyclopropenium ion to the coordinated polyolefin.

The reactions of substituted cyclopropenium ions, $[C_3R_3]^+$, with transition metal substrates [1] lead to the formation of η^3-cyclopropenyl complexes, e.g. $[Ni(\eta^3\text{-}C_3Ph_3)(PPh_3)_2]^+$ [2], η^3-oxocyclobutenyl derivatives, e.g. $[Co(CO)_3(\eta^3\text{-}C_3Ph_3CO)]$ [3] or metallacyclobutanes, e.g. $[RhCl_2(PMe_2Ph)_2\text{-}(C_3Ph_3)]$ [4]. In only one case has C—C bond formation been reported, viz. in the synthesis of the substituted cyclopentadienyl complex $[MH(CO)_3\text{-}\{\eta^5\text{-}C_5H_4(C_3Bu^t{}_3)\}]$ from $[C_3Bu^t{}_3]^+$ and $[M(CO)_3Cp]^-$ (M = Mo or W) [5]. We now describe a reaction in which polycyclic alkene formation occurs between ring-opened $[C_3Ph_3]^+$ ions and coordinated cyclooctatetraene (COT).

In CH_2Cl_2, $[Fe(CO)_3(\eta^4\text{-COT})]$ and $[C_3Ph_3][BF_4]$ yield a yellow-brown solution from which the yellow salt $[Fe(CO)_3(C_8H_8C_3Ph_3)][BF_4]$ (I: 46%, $\tilde{\nu}(CO)$ (CH_2Cl_2) 2104, 2056, and 2042 cm^{-1}) was isolated. The complex ^1H NMR spectrum could not be satisfactorily assigned but suggested C—C bond formation between the three- and eight-membered rings. In the absence of suitable crystals for X-ray structural studies, complex I was treated with $Na[BH_4]$ in THF to yield the yellow, neutral compound $[Fe(CO)_3\text{-}(C_8H_9C_3Ph_3)]$ (II: 25%, $\tilde{\nu}(CO)$ (hexane) 2052, 1989, and 1985(sh) cm^{-1}), which was successfully crystallised from n-hexane at —78°C. An X-ray diffraction study on II revealed annelation of the ring-opened cyclopropenium ion to the eight-membered ring via three new carbon—carbon bonds.

Crystal data: $C_{32}H_{24}FeO_3$, $M = 512$, monoclinic, space group $P2_1/n$, $Z = 4$, a 13.651(6), b 12.744(3), c 14.932(6) Å, β 107.35(3)°, U 2479.5(5) Å^3, $F(000) = 1064$. The structure was solved by heavy-atom methods from data collected in the range $2.9 \leqslant 2\theta \leqslant 55°$ on a Syntex $P2_1$ diffractometer with monochromatised Mo-K_α X-radiation. For the 2484 (total 4673) reflections ($I \geqslant 3.0\sigma(I)$), with anisotropic thermal parameters for all non-hydrogen atoms, and with hydrogen atoms refined isotropically, $R = 0.073$ ($R' = 0.077$).

The structure of II is illustrated in Fig. 1, together with the atom numbering

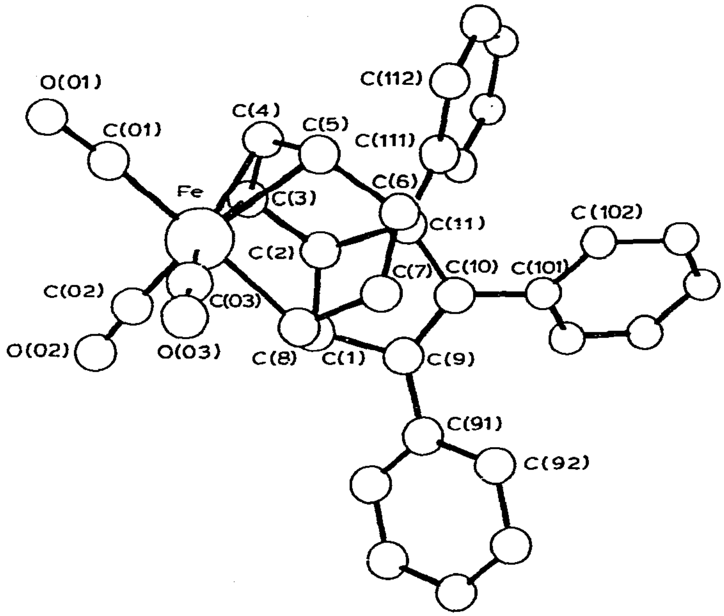


Fig. 1. Molecular structure of [$Fe(CO)_3\{\sigma,\eta^3\text{-}C_8H_9(C_3Ph_3)\}$].

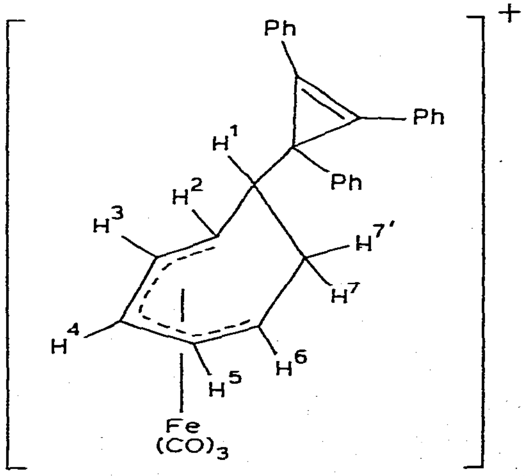
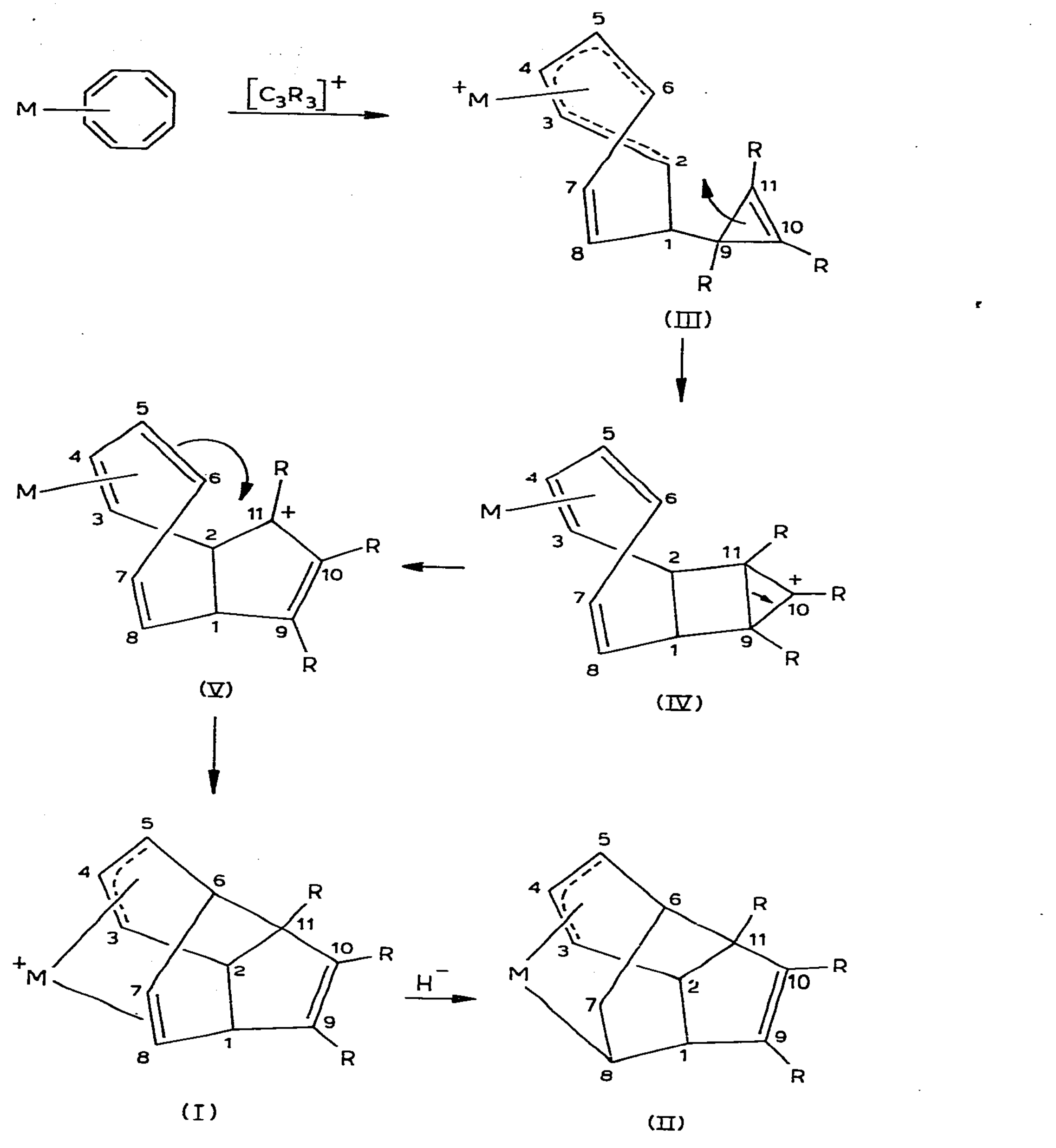


Fig. 2.



SCHEME 1. M = Fe(CO)$_3$, R = Ph.

system. The iron atom is in a distorted octahedral configuration, η^3-bonded to the eight-membered ring (C(1)—C(8)) via carbon atoms C(3)—C(5) (Fe—C-(mean) 2.159(6), C—C(mean) 1.38(1) Å) and σ-bonded to C(8) (Fe—C(8) 2.122(6) Å), and carrying three linear carbonyl ligands. The ring-opened cyclopropenium ion, C(9)—C(11), has joined to the eight-membered ring so that C(9) is bonded to C(1) and C(11) is bonded to both C(2) and C(6). This generates a cyclopentene ring (C(2),C(1),C(9)—C(11)) with the double bond between C(9) and C(10) (1.359(8) Å) and a mean C—C distance for the other four bonds of 1.537(8) Å, a cyclohexane (chair ring (C(1),C(2),C(11),C(6)—C(8); C—C(mean) 1.534(8) Å) and a second six-membered ring (C(2)—C(6), C(11)) which includes the η^3-allyl group. The ^{1}H NMR spectrum of II shows that hydride addition to I occurs at C(7).

The mechanism proposed for the formation of I is shown in Scheme 1. Initial attack of the $[C_3Ph_3]^+$ ion at C(1) forms the cyclopropenyl-substituted cyclooctatetraenyl complex III. Nucleophilic attack by the PhC=CPh double bond at the terminal carbon atom, C(2), of the pentadienyl group yields carbonium ion IV which undergoes cyclopropane ring-opening to give V. Carbon—carbon bond formation between C(6) and C(11) completes the synthesis. Evidence for the first step of the sequence is provided by the isolation of low yields of yellow $[Fe(CO)_3\{\eta^5\text{-}C_7H_8(C_3Ph_3)\}][BF_4]$ (VI: 6%, $\tilde{\nu}$(CO) (CH_2Cl_2) 2113 and 2057 cm^{-1}) from $[Fe(CO)_3(\eta^4\text{-cycloheptatriene})]$ and $[C_3Ph_3][BF_4]$. The ^{1}H NMR spectrum (acetone-d_6, δ 7.4—7.0, Ph and H^4; 6.44, H^5; 6.17 H^3; 5.49 H^6; 5.03 H^1 and H^2; 4.35 and 4.03 H^7 and H$^{7'}$) shows VI to have the structure shown in Fig. 2.

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