

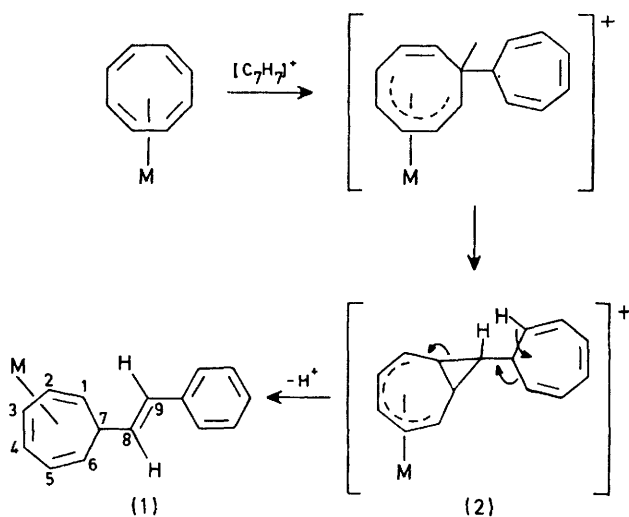
## Reaction of $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ (cot = cyclo-octatetraene) with the Tropylium Ion: Unusual Rearrangement of Cyclo-octatetraene and Cycloheptatriene Rings and the X-Ray Crystal Structure of $[\text{Fe}(\text{CO})_3(\eta^4\text{-styryl-cycloheptatriene})]$

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**Summary** The tropylium ion  $[\text{C}_7\text{H}_7]^+$  reacts with  $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$  (cot = cyclo-octatetraene) to give  $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{15}\text{H}_{14})]$ , X-ray studies of which reveal a styrylcycloheptatriene ligand; the  $\text{C}_7$ -ring originates from the co-ordinated cot, the phenyl group from the tropylium ion.

DURING studies of the reactions between organotransition-metal complexes and one-electron oxidants<sup>1</sup> we have investigated the reaction between  $[\text{Fe}(\text{CO})_{3-n}\{\text{P}(\text{OMe})_3\}_n(\eta^4\text{-cot})]$  ( $n = 0-2$ ) (cot = cyclo-octatetraene) and the tropylium ion  $[\text{C}_7\text{H}_7]^+$ . Unsubstituted  $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$  affords a complex of styrylcycloheptatriene *via* an unusual rearrangement involving both the  $\text{C}_8$ - and  $\text{C}_7$ -rings of the reactants.



In acetone at  $-23^\circ\text{C}$   $[\text{C}_7\text{H}_7][\text{BF}_4]$  and  $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$  give an orange solution from which pale yellow crystals of  $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{15}\text{H}_{14})]$  may be obtained [(1), 32%,<sup>†</sup> m.p.  $64-66^\circ\text{C}$ ,  $\bar{\nu}(\text{CO})(\text{hexane})$  2046, 1986, and  $1974\text{ cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\tau$  2.70 (5 H, m, Ph), 3.57 (1 H, d,  $J_{8\text{-H},9\text{-H}}$  16 Hz, 9-H), 4.14 (1 H, ddd, 5-H), 4.15 (1 H, dd,

8-H), 4.64 (2 H, m, 2-H and 3-H), 4.87 (1 H, ddd, 6-H), 6.75 (2 H, m, 1-H and 7-H), and 6.95 (1 H, dddd, 4-H)].<sup>‡</sup> The unexpected identity of (1) was established by an X-ray diffraction study which also made possible a rationalisation of the  $^1\text{H}$  n.m.r. spectrum.

**Crystal data:**  $\text{C}_{18}\text{H}_{14}\text{FeO}_3$ ,  $M = 334$ , monoclinic, space group  $C2/c$ ,  $a = 25.035(8)$ ,  $b = 6.195(2)$ ,  $c = 20.938(12)$  Å,  $\beta = 102.69(4)^\circ$ ,  $U = 3168(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $F(000) = 1376$ . The structure was solved by heavy-atom methods from data collected to  $2\theta = 55^\circ$  on a Syntex  $P2_1$  four-circle diffractometer with monochromatised  $\text{Mo-K}\alpha$  X-radiation. For the 1977 observed reflections [ $I \geq 1.5\sigma(I)$ ], and with anisotropic thermal parameters for all non-hydrogen atoms,  $R = 0.063$ ,  $R^1 = 0.047$ .<sup>§</sup> The X-ray structural study reveals the presence of a styrylcycloheptatriene ligand with the 7-styryl substituent *exo* to the  $\eta^4$ -bonded  $\text{Fe}(\text{CO})_3$  group. As might be expected (Figure) the atom sequences C(7)—C(15), which includes the styryl group, and C(1)—C(4) of the  $\eta^4$ -bonded  $\text{C}_7$ -ring, are each coplanar.

Although u.v. photolysis of free cot yields styrene,<sup>2</sup> the styryl group in (1) does not originate from the cot ligand.

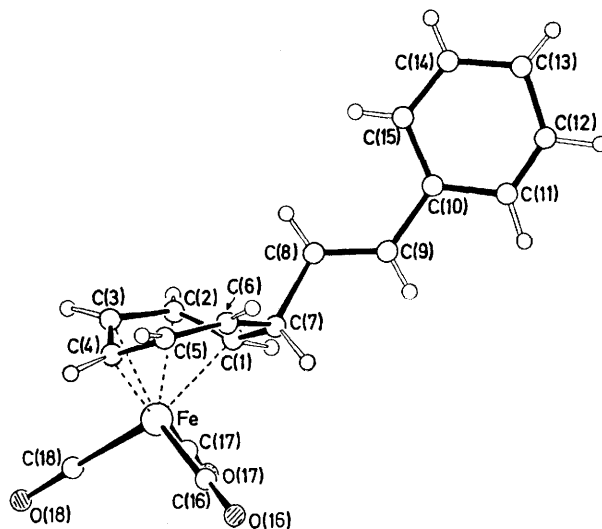


FIGURE. Molecular structure of  $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{15}\text{H}_{14})]$ .

<sup>†</sup> The yield is increased (41%) in the presence of pyridine.

<sup>‡</sup> For the sake of brevity coupling constants, determined by  $^1\text{H}$ - $^1\text{H}$  decoupling of the 200 MHz  $^1\text{H}$  n.m.r. spectrum, are omitted.

<sup>§</sup> The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The proposed mechanism for the formation of (1) (Scheme) avoids the necessity for  $\text{Fe}(\text{CO})_3$  migration, required if isomerisation of the  $\text{C}_8$ -ring to a styrene derivative occurs. Initial addition of  $[\text{C}_7\text{H}_7]^+$  to the cot ligand is followed by isomerisation to the bicyclo[5.1.0]octadienyl complex (2). Spontaneous deprotonation followed by a rearrangement similar to that proposed in the preceding communication gives (1).

Evidence for this mechanism is provided by the identity of the product formed from  $[\text{C}_7\text{H}_7]^+$  and  $[\text{Fe}(\text{CO})_3(\eta^4\text{-methylcyclo-octatetraene})]$ . The  $^1\text{H}$  n.m.r. spectrum of yellow, crystalline  $[\text{Fe}(\text{CO})_3\{\eta^4\text{-C}_{15}\text{H}_{13}(\text{Me})\}]$  [ $^1\text{H}$  n.m.r.

( $\text{CDCl}_3$ )  $\tau$  2.70 (5 H, m, Ph), 3.55 (1 H, d, 9-H), 4.28 (1 H, dd, 8-H), 4.32 (1 H, d, 5-H), 4.70 (2 H, m, 2-H and 3-H), 6.75 (1 H, m, 1-H), 6.90 (1 H, m, 4-H), 6.97 (1 H, m, 7-H), and 8.51 (3 H, dd,  $J_{\delta\text{-H,Me}}$  1.4 Hz,  $J_{7\text{-H,Me}}$  0.8 Hz, Me)] reveals the methyl group bonded to C-6 of the cycloheptatriene ring.

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<sup>1</sup> K. Amos and N. G. Connelly, *J. Organomet. Chem.*, 1980, **194**, C57, and references therein.

<sup>2</sup> G. I. Fray and R. G. Saxton, 'The Chemistry of Cyclo-octatetraene and its Derivatives,' Cambridge University Press, 1978, p. 18.

<sup>3</sup> N. G. Connelly, R. M. Mills, M. W. Whiteley, and P. Woodward, preceding communication.