

## $\eta^2$ -Cyclo-octatetraene: Crystal and Molecular Structure of $[\text{Mn}(\text{CO})_2(\eta^2\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)]$

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**Summary** N.m.r. and X-ray diffraction studies have established that in  $[\text{Mn}(\text{CO})_2(\eta^2\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)]$  there exists the first example of cyclo-octatetraene co-ordinated in an unequivocally  $\eta^2$ -mode.

CYCLO-OCTATETRAENE, in its drastically modified reactivity upon co-ordination, in the wide variety of its modes of co-ordination, and in the proliferation of fluxional behaviour among its complexes, has played an important role in the development of organo-transition metal chemistry. Complexes are known in which the hydrocarbon is  $\eta^3$ -,  $\eta^4$ - (three modes),  $\eta^6$ -, and  $\eta^8$ -co-ordinated with a transition metal, but none has been described containing an authentic  $\eta^2$ -cyclo-octatetraene ligand, the simplest possible mode. Catenated  $[\text{CuCl}(\text{C}_8\text{H}_8)]^\dagger$  is sometimes described as having  $\eta^2$ -cyclo-octatetraene, but there are strong structural indications that copper is involved in significant interaction with two double bonds of the olefin. The frequent invoking<sup>2</sup> of a transient  $\eta^2$ -mode for cyclo-octatetraene, and the possibility of unique fluxional behaviour of such a species, led us to synthesise  $[\text{Mn}(\text{CO})_2(\eta^2\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)]$ .

U.v. irradiation of a tetrahydrofuran (THF) solution of  $[\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$  yields well known red  $[\text{Mn}(\text{CO})_2(\text{THF})(\eta^5\text{-C}_5\text{H}_5)]$ , which, on treatment with cyclo-octatetraene and subsequent chromatographic purification, provides  $[\text{Mn}(\text{CO})_2(\eta^2\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)]$  as orange crystals [20%; m.p. 68 °C (decomp.);  $\nu_{\text{CO}}$  (hexane) 1971s and 1915s  $\text{cm}^{-1}$ , moderately stable in air, but very oxygen-sensitive in

solution. Proton [ $\tau$  3.82 (m, 2H), 4.49 (m, 4H), 6.07 (s, 5H), and 6.86 (m, 2H)] and  $^{13}\text{C}$  [234.9 (CO), 133.6, 126.8, 124.8, 86.3 ( $\text{C}_5\text{H}_5$ ), and 56.9 p.p.m. (downfield of  $\text{Me}_4\text{Si}$ )] n.m.r. spectra clearly indicate the co-ordination to manganese of only one olefinic bond of cyclo-octatetraene, a feature unequivocally established by an X-ray diffraction study (Figure).†

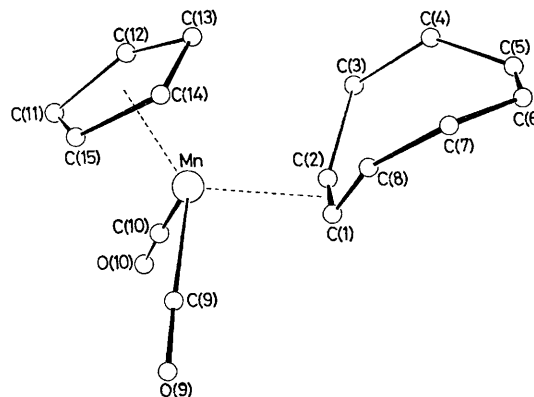


FIGURE. Molecular structure of  $[\text{Mn}(\text{CO})_2(\eta^2\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)]$ . Bond lengths are: Mn-C(1), 2.193(2); Mn-C(2), 2.202(2); C(1)-C(2), 1.398(2); C(2)-C(3), 1.479(2); C(3)-C(4), 1.340(3); C(4)-C(5), 1.464(3); C(5)-C(6), 1.342(3); C(6)-C(7), 1.461(3); C(7)-C(8), 1.337(3); C(8)-C(1), 1.484(2) Å.

† 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.

Crystals of  $[\text{Mn}(\text{CO})_2(\eta^2\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)]$  are monoclinic, space group  $P2_1/c$ ,  $a = 10.813(7)$ ,  $b = 6.606(4)$ ,  $c = 17.164(9)$  Å,  $U = 1222(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 576$ ,  $\mu(\text{Mo-K}\alpha) = 9.9$  cm<sup>-1</sup>. The structure was solved by conventional heavy-atom methods from data collected on a Syntex  $P2_1$  4-circle diffractometer to  $2\theta_{\text{max}} = 55^\circ$ . For the 2787 independent reflections [ $I \geq 1.0\sigma(I)$ ],  $R = 0.034$ .†

The manganese atom is in almost ideal octahedral co-ordination, the cyclopentadienyl ring employing three facial sites and the two carbonyls one site each, with the remaining site occupied by a double bond of the tetraene. The molecule possesses a (non-crystallographic) plane of symmetry which bisects the  $\text{Mn}(\text{CO})_2$  angle and passes through C(13) and the midpoints of the C(1)-C(2) and C(5)-C(6) bonds. The folds in the  $\text{C}_8$  ring along C(3) ··· C(8) and C(4) ··· C(7) produce dihedral angles of *ca.* 143 and 147° respectively, while the  $\text{MnC}(1)\text{C}(2)$  plane makes a dihedral angle of *ca.* 106° with the C(1)C(2)C(3)C(8) portion of the ring. The cyclo-octatetraene ligand thus presents the convex face of a tub conformation towards the cyclopentadienyl ring.

Free cyclo-octatetraene undergoes a rapid bond-shift isomerisation<sup>3</sup> which is evidently quenched on co-ordination of the  $[\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$  species to one olefinic bond. At ambient temperature the n.m.r. spectra of the complex are compatible only with a stereochemically rigid molecular

structure. Efforts to induce a migration of the metal grouping about the  $\text{C}_8\text{H}_8$  ring, such as occurs with  $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_8\text{H}_8)]$  and  $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_8\text{H}_8)]$ , were thwarted by decomposition of the complex at higher temperatures, the products being cyclo-octatetraene and red  $[\{\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}_2\text{C}_8\text{H}_8]$ . Initial studies of the chemistry of  $[\text{Mn}(\text{CO})_2(\eta^2\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)]$  suggest high lability for the  $\eta^2\text{-C}_8\text{H}_8$  ligand, which is rapidly displaced by phosphines at room temperature.

A complex of cycloheptatriene as an  $\eta^2$ -ligand is produced by a route identical to that described above. The <sup>13</sup>C n.m.r. spectrum [235.5 (CO), 233.9 (CO), 137.8, 131.0, 128.2, 84.0 ( $\text{C}_5\text{H}_5$ ), 53.6, 52.6, and 34.0 p.p.m.] of yellow crystalline  $[\text{Mn}(\text{CO})_2(\eta^2\text{-C}_7\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)]$  [m.p. 59 °C (decomp);  $\nu_{\text{CO}}$  (hexane) 1965s and 1909s cm<sup>-1</sup>] accords with co-ordination of cycloheptatriene through an olefinic bond adjacent to the ring methylene carbon. It should be noted that irradiation of  $[\text{Mn}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$  in the presence of cycloheptatriene or cyclo-octatetraene in non-co-ordinating solvents has been reported<sup>4</sup> to effect complete carbonyl substitution and formation of the appropriate  $\eta^6$ -olefin complex.

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