A New Transformation of Cyclo-octatetraene upon Complexation: Crystal and Molecular Structure of Two Isomers of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$

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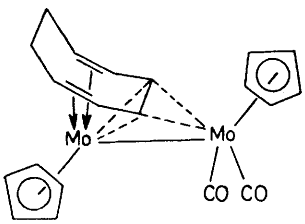
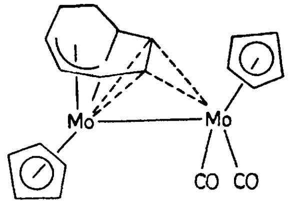
Summary Cyclo-octatetraene reacts with $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ in octane at reflux to give purple $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$, which in polar solvents undergoes a hydrogen shift within the C_8 ring to yield an orange isomer; *X*-ray diffraction studies have established the molecular structure of each isomer.

CERTAIN carbonylruthenium complexes promote dehydrogenative ring-closure of cyclo-octatetraene, thereby affording complexes of pentalene.[1] In attempting to extend this transformation to other metals, we have investigated the reaction of cyclo-octatetraene with $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, a carbonyl whose reactions with polyolefins have been little studied but which contains the di-metal unit required for pentalene co-ordination. No such complex was produced. Instead an unprecedented rearrangement of cyclo-octatetraene occurred, leading to the discovery of two new modes of co-ordination of a C_8 ring across a metal–metal bond.



(1)



(2)

Heating $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ at reflux with an excess of C_8H_8 in octane yields purple crystalline $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ [(**1**); m.p. 151—153 °C (decomp.); ν_{CO} (hexane) 1932s and 1870s cm^{-1}] which is apparently formed *via* the Mo–Mo triply bonded species $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2]$.[2] Thus, heating $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ in octane generated i.r. bands characteristic of the tetracarbonyl, and these were replaced by bands due to (**1**) on addition of cyclo-octatetraene. The ^1H n.m.r. spectrum† of (**1**) revealed pairwise equivalence of the C_8 ring protons, four of which have shifts typical of an aliphatic environment. The proton-coupled ^{13}C n.m.r. spectrum‡ is in agreement and clearly indicates that two of the C_8 ring carbon atoms are no longer carrying protons. This evidently unique rearrangement of cyclo-octatetraene on complexation called for an *X*-ray diffraction study.

Crystal data: (**1**); $C_{20}H_{18}Mo_2O_2$, *M* 482, monoclinic, space group $P2_1/c$, $a = 8{\cdot}629(2)$, $b = 39{\cdot}580(10)$, $c = 15{\cdot}759(7)$ Å, $\beta = 103{\cdot}90°$, $Z = 12$. Data were collected on a Syntex $P2_1$ four-circle diffractometer to $2\theta = 50°$ (Mo-K_α *X*-radiation) and the structure solved by heavy-atom methods, with refinement using anisotropic thermal parameters for Mo and O atoms only. For the 4164 independent reflections, $R = 0{\cdot}079$.

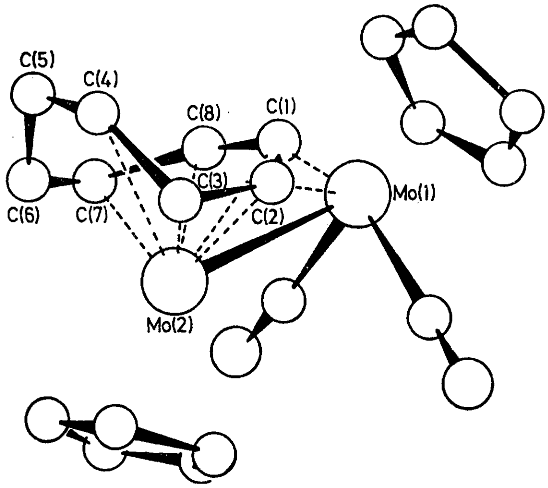


FIGURE 1. Molecular structure of purple $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (**1**): Mo(1)–Mo(2) (mean), 3·057(3); Mo(1)–C(1) (mean), 2·12(3); Mo(1)–C(2) (mean), 2·10(3); Mo(2)–C(1) (mean), 2·19(3); Mo(2)–C(2) (mean), 2·18(3); Mo(2)–C(3) (mean), 2·18(3); Mo(2)–C(4) (mean), 2·26(4); Mo(2)–C(7) (mean), 2·30(3); and Mo(2)–C(8) (mean), 2·19(3) Å.

The structure (Figure 1) is especially interesting crystallographically in that there are three distinct molecules in the asymmetric unit, though these are, within experimental error, all identical in their molecular parameters.

The determination shows that in (**1**) the C_8 ring is retained, in contrast to the recent observation of a ring opening of C_8H_8 in a di-ruthenium complex,[3] and that two hydrogen atoms appear to have undergone a 1,4-migration within the ring. Atoms C(1) and C(2), devoid of hydrogen atoms, form a symmetric transverse bridge perpendicular to a Mo–Mo bond, with a pair of atoms to either side of the bridge [C(3)–C(4) and C(7)–C(8)] bonded to one molybdenum, leaving methylenic carbons C(5) and C(6) non-bonded. Although delocalisation in the η^6-system is evident, the structure is perhaps most easily appreciated when represented as a combination of bridging acetylene and η^2-olefin units, as shown.

Although stable in benzene, carbon tetrachloride, or alkanes, in polar solvents (**1**) isomerises to an orange form (**2**) [m.p. 133—134 °C; ν_{CO}(hexane) 1930s and 1866s cm^{-1}] with an identical mass spectrum but with different n.m.r. spectra.§ An *X*-ray diffraction study has shown (Figure 2)

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† $\tau(C_6D_6)$ 4·28 (2H, d), 4·80 (5H, s), 5·26 (5H, s), 6·65 (2H, m), 8·12 (2H, m), and 8·70 (2H, m).

‡ Downfield of Me_4Si, 35·25 (t, $2\times CH_2$), 65·83 (d, $2\times CH$), 89·07 (d, C_5H_5), 92·28 (d, C_5H_5), 100·47 (d, $2\times CH$), and 119·10 (s, 2 C) p.p.m.

§ ^1H (220 MHz, $CDCl_3$): τ 3·48 (1H, d of t), 4·60 (5H, s), 4·70 (1H, s), 5·18 (5H, s), 5·74 (1H, dd), 7·43 (1H, m), 7·55 (1H, q), 7·77, (1 H, t of dd), 8·50 (1H, m), and 10·97 (1H, m); ^{13}C (C_6D_6): 23·54 (t, CH_2), 43·62 (t, CH_2), 59·76 (d, CH), 78·14 (d, CH), 88·82 (d, C_5H_5), 91·80 (d, CH), 92·46 (d, C_5H_5), 98·84 (s, C), 107·94 (d, CH), and 123·47 (s, C) p.p.m.

that the isomerisation involves hydrogen migration within the C_8H_8 ring.

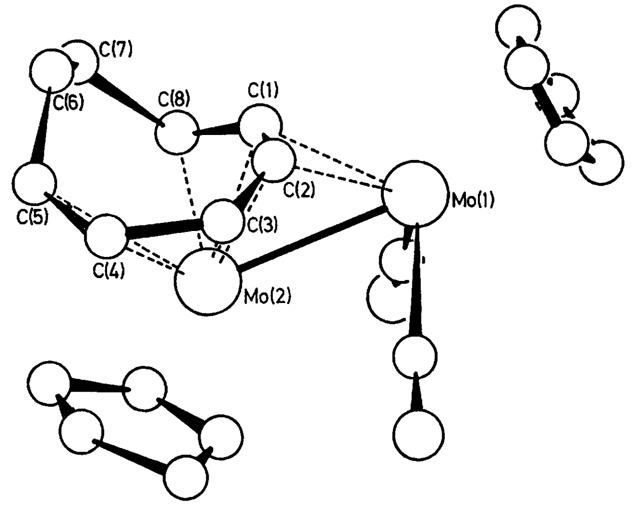

FIGURE 2. Molecular structure of orange $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (**2**): Mo(1)–Mo(2), 3·032(3); Mo(1)–C(1), 2·12(1); Mo(1)–C(2), 2·12(2); Mo(2)–C(1), 2·16(1); Mo(2)–C(2), 2·17(2); Mo(2)–C(3), 2·23(2); Mo(2)–C(4), 2·26(2); Mo(2)–C(5), 2·29(2); and Mo(2)–C(8), 2·28(2) Å.

Crystal data: (**2**); $C_{20}H_{18}Mo_2O_2$, *M* 482, monoclinic, space group $P2_1/n$, $a = 8{\cdot}150(3)$, $b = 11{\cdot}978(9)$, $c = 17{\cdot}529(10)$ Å, $\beta = 92{\cdot}28(4)°$, $Z = 4$. Data were collected and the structure solved as for (**1**); refinement was with anisotropic thermal parameters for the Mo atoms only. For the 2095 independent reflections $R = 0{\cdot}084$.

The $Mo_2(CO)_2(\eta\text{-}C_5H_5)_2$ skeleton of orange (**2**) is essentially identical with that of the purple isomer (**1**), and the C_8 ring is again attached to both Mo atoms by a transverse acetylenic bridge. The further bonding of the ring to one molybdenum atom is, however, more asymmetric than in (**1**) and can be visualised in (**2**) as an η^3-allyl interaction of C(3)–C(5) on one side of the bridge, and an η^1-interaction of C(8) on the other. Bond lengths and planarity of the η^6-system point to extensive delocalisation, which is emphasised by the high field shift [τ 10·97 (1H)] observed in the n.m.r. spectrum. This we attribute to the proton of the methylenic carbon C(6) which is held (Figure 2) above the η^6-system. Similar shifts have been observed for the aliphatic proton held above the postulated homotropylium C_7-6π system in $[Mo(CO)_3(\eta^7\text{-}C_8H_9)]^+$ (τ 10·14)[4] and in $[C_8H_9]^+$(τ 10·67).[5] However, the implication that orbital overlap between C(5)–C(8) allows a ring current in a homoaromatic C(1)–C(5) and C(8) electronic system co-ordinated to Mo(2) is tempered by the C(5)–C(8) distance of 2·52 Å.

In various polar solvents the irreversible isomerisation is first order in (**1**), suggesting a simple intramolecular hydrogen shift process. Of the two hydrogen shifts [C(8) → C(2) and C(5) → C(7)] which directly convert (**1**) into (**2**) we favour the latter, which does not require a disruption of the Mo_2C_2 bridging unit. The rate of isomerisation is strongly solvent dependent; least-squares fits of straight lines to data obtained by ^1H n.m.r. spectroscopy give concentration-independent half-lives for (**1**) of 6 min (CD_2Cl_2) and 31 min ($CDCl_3$). In $(CD_3)_2CO$ the half-life is very sensitive to the degree of water impurity, with variation from 1340 min in rigorously dried solvent down to 13 min when untreated. The presence of traces of CF_3CO_2H has a more dramatic and catalytic effect; even in benzene, in which (**1**) is otherwise stable, near instantaneous isomerisation occurs. However, use of CF_3CO_2D or D_2O in deuteriated solvents on no occasion results in deuterium incorporation into (**2**).

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