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# Transition Metal Complexes and the Mechanism of Pentalene Formation

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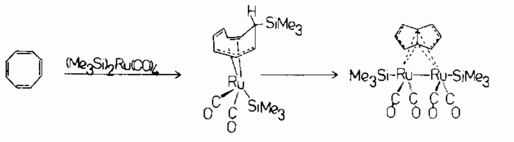
*The dehydrogenative transannular ring closure of cyclooctatetraenes to pentalenes is rationalised on the basis of a disrotatory electrocyclisation of a cyclooctadienyl moiety; the bridgehead hydrogens, now* syn *to a coordinatively unsaturated metal atom, are lost by a series of oxidative addition and reductive elimination processes.*

The recent isolation by Knox, Stone and their coworkers of pentalene complexes of ruthenium via the dehydrogenative transannular ring closure of cyclooctatetraene (COT) has been an exciting development in organometallic chemistry [1].



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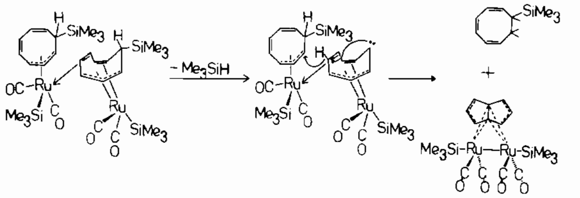
The possibility of using transition metal complexes for the large scale preparation of pentalene derivatives is attractive, and to this end an understanding of the mechanism of ring closure would be greatly advantageous. A tentative proposal [2] invoking transannular attack by a carbene is shown in Scheme I:



Scheme I

Such a proposal, however, is untenable for several reasons. Firstly, the unprecedented α-elimination of $Me_3SiH$ from 2 to produce the carbene is a somewhat improbable process. The seemingly analogous [3] elimination of $Me_3SiF$ to produce the $CHF_2\cdot\ddot{C}F$ carbene is not in fact the relevant comparison claimed by Harris *et al.* [2]. Thus, the latter process is a high temperature (>300 °C) gas phase elimination leading to the formation of a 560 kJ/mol silicon–fluorine bond; the process postulated in scheme I occurs even in refluxing heptane and yields only a 310 kJ/mol Si–H bond. Secondly, in the improbable circumstance that one generated a carbene intermediate, the transannular attack is unlikely to compete successfully with hydrogen abstraction or with collapse of the vinyl carbene to an allene. Finally, such an α-elimination mechanism is not applicable to the closely related reaction of COT with $Ru_3(CO)_{12}$ which also yields a pentalene complex [4]. Clearly, a mechanistic rationale is needed which accounts not only for these experimental data but also for other related molecules.

We note initially that, in 1969, Bates [5] reported the transannular cyclisation of the octadienyl anion, *4*, to the bicyclo[3.3.0]octenyl anion, *5*. This reaction, as predicted by orbital symmetry considerations [6], is a disrotatory 6π electrocyclisation. Now, examination of the fluxional intermediate *2* reveals an exactly analogous situation to that in the Bates reaction; however, the disrotatory ring closure can yield isomers in which the metal is either *syn, 6,* or *anti, 7,* to the bridgehead hydrogens, and this must be analysed further.

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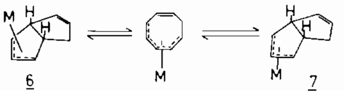

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Recently, Pinhas and Carpenter have proposed a general scheme for transition metal promoted electrocyclic reactions [7]. This approach utilises the symmetry of the HOMO of the reactant with respect to the plane bisecting the breaking σ-bond to indicate which disrotatory mode will be favored. Now, applying these ideas to a system such as cyclopentenyl manganese tricarbonyl, we see that the situation closely parallels that previously described for the

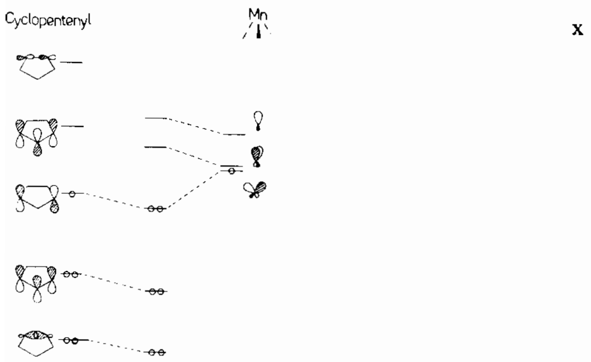
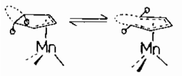


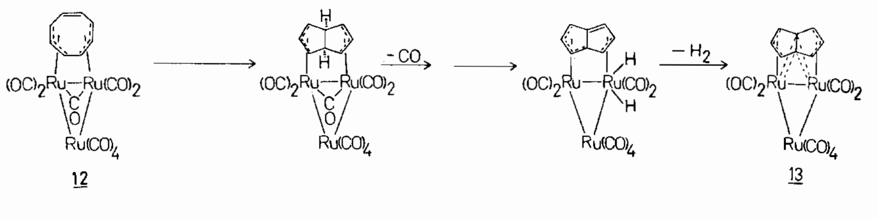
Fig. 1. Molecular orbital scheme.

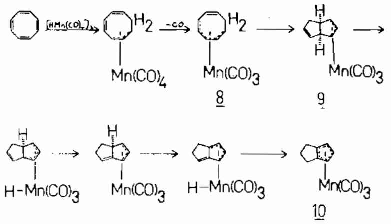
cyclobutene iron tricarbonyl system in which the hydrogens *syn* to the metal rotate outwards in a disrotatory process. Indeed Fig. 1 is constructed by analogy to the one presented for *cyclo*-$C_4H_6Fe(CO)_3$ in Ref. 7. It is apparent that the HOMO is antisymmetric with respect to the plane bisecting the breaking σ-bond, and thus the preferred motion is bending of the σ-bond towards the metal pushing both the *syn*-hydrogens outwards.



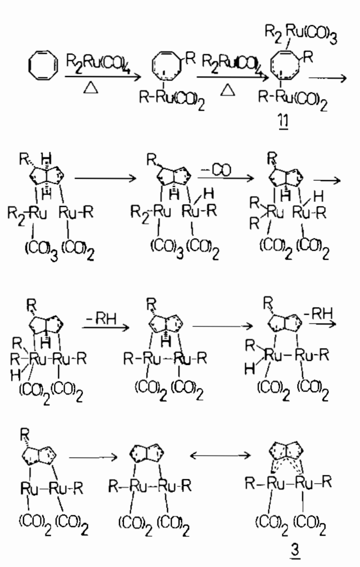
Such a mechanism readily explains the production of the bicyclo[3.3.0]octadienyl system, *10*, from COT and $[HMn(CO)_4]_3$ [8]. Thus, after formation of the necessary pentadienyl system *8*, and ring closure to *9*, the coordinatively unsaturated manganese atom is now well situated for oxidative addition by insertion into a bridge-head C–H linkage. The requisite hydrogen migrations are outlined in Scheme II.

It is now apparent that the key to pentalene production is the electrocyclisation of an intermediate such as *11*, thereby positioning the bridgehead hydrogens so as to facilitate their oxidative addition to the coordinatively unsaturated ruthenium atom; subsequent reductive elimination of trimethylsilane leads to the pentalene complex *3* as shown in Scheme III. Of course, one could vary the sequence of oxidative additions and reductive eliminations shown in Scheme III; the crucial point is that after the electrocyclic ring closure all the proposed steps





Scheme II



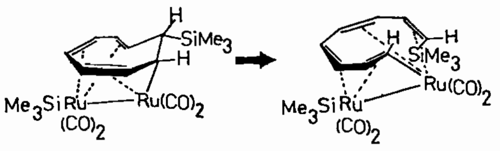
R = $SiMe_3$, $GeMe_3$

Scheme III

are well precedented and merely involve the normal 16-electron–18-electron exchange sequences so prevalent at Group VIII metal centres [9]. The particular sequence chosen in this case is not germane to the current discussion.

Likewise, the pentalene product [4] from COT and $Ru_3(CO)_{12}$ *viz. 13*, can be derived by disrotatory electrocyclisation of *12*. Indeed such processes are quite general phenomena as exemplified by the cobalt-promoted cyclisation reported by Otsuka and Taketomi [10].

In a related system, the complex $(C_8H_8SiMe_3)$-$Ru_2(CO)_5SiMe_3$, when heated in octane loses CO to produce *14* which opens to the octatetraene complex *15* [11]. The Pinhas–Carpenter approach [7] would suggest the favored process to be a 'disrotatory-towards' ring opening, but with the proviso that a con-rotatory opening may be a serious contender. In fact the latter circumstance obtains and the reaction has the appearance of a conventional [6] thermally allowed 8$\pi$ cycloreversion but with $\pi$-bonded impedimenta rather than $\sigma$-bonded substituents.



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To summarise therefore; the elegant Knox–Stone dehydrogenative transannular ring closure of cyclooctatetraenes to pentalenes occurs when a metal–cyclooctatrienyl moiety electrocyclises in a disrotatory manner thus rendering the metal atom coordinatively unsaturated; the bridge-head hydrogen atoms can now oxidatively add to the 16-electron metal atoms and subsequent reductive elimination steps produce pentalene complexes.

## Acknowledgment

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