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NON-RIGID MOLECULES

III*. SIGMATROPISM IN ORGANOMETALLIC COMPLEXES OF INDENE

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SUMMARY

The effects of π system geometry upon the transition states for sigmatropism in five-membered rings is discussed semi-quantitatively using the PMO theory. Comparison of the results with measured activation energies suggests that the [1, 3] averaging in organometallic indene complexes proceeds via sequential [1, 2] shifts in all those cases examined.

The fluxional processes in σ-bonded organometallic complexes of cyclopentadiene are quite well characterised experimentally[2-4] and theoretically[5-7] as concerted intramolecular [1, 5] sigmatropic shifts. In analogous cycloheptatriene complexes, where [1, 5] shifts can be distinguished from the least motion [1, 2] path, the former have been shown to predominate[8]. This important result indicates the usefulness of orbital symmetry arguments in this area. Our present purpose is to consider, in a semiquantitative manner, the effects of π system geometry upon the transition states for sigmatropic shifts in five-membered rings. Only 1-indenyl complexes will be considered explicitly, although the method is capable of obvious extension to other systems.

In the transition state for suprafacial [1, 5] migration with retention of configuration[5], the σ-bonding orbital of the migrating group lies in the nodal plane of a 3-centre non-bonding orbital formed from the p_π orbitals of carbon atoms at the origin and terminus. The nodal plane of this orbital, of course, bisects the [1, 5] C–C bond. If the adjacent delocalized π system has a non-bonding molecular orbital (NBMO) of the correct nodal properties, a strong first order interaction will occur, stabilizing the transition state and facilitating the motion. Moreover *d* orbitals centred on the migrating atom can also mix into this critical orbital (Fig. 1). However this interaction will only further stabilize the transition state if the *d* orbitals concerned are empty and relatively low-lying in energy.

In the cyclopentadienyl ring the adjacent π system forms an odd alternant network resembling allyl, while in the indenyl ring it resembles benzyl. The relevant NBMO coefficients are found[9] to be $1/\sqrt{2}$ and $-1/\sqrt{2}$ in the former case, and $2/\sqrt{7}$

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* For Part II see ref. 1.

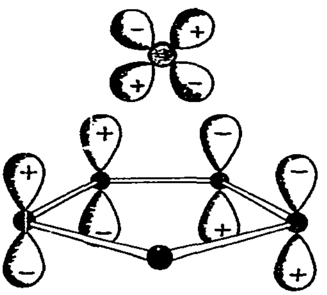
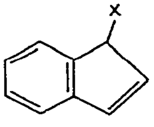
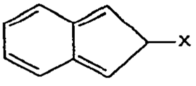


Fig. 1. Orbital phases for overlap between ring antisymmetric π orbitals and d orbital of the migrating atom.

and $-1/\sqrt{7}$ in the latter. The corresponding ratio of first order interaction energies is estimated[10] to be $3/\sqrt{14}$ (~ 0.8). In other words, a transition state of the type shown in Fig. 1 should be only slightly less stable ($\sim 20\%$ total interaction energy) in the indenyl than in the cyclopentadienyl ring system. This supports the view[6,7,11] that the large (though not accurately known) sigmatropic activation energy difference between analogous indenyl and cyclopentadienyl complexes is due to the participation of an unfavourable valence tautomer of indene (II).



(I)



(II)

It is of interest to estimate the energy difference between (I) and (II) as accurately as possible within the context of the present approximations. Either π system may be formally derived from benzyl by union of a methylene group. Direct perturbational calculation[10] of the corresponding first order energy difference gives $2\beta/\sqrt{7}$ (~ 13.1 kcal · mol^{-1})*. An alternative approach is to calculate separately the total π energies of (I) and (II) and subtract them. Values of 9.4 and 8.6 kcal · mol^{-1} have been obtained[11] in this way. For reasons discussed elsewhere[10] we tentatively prefer the direct calculation and its result of ~ 13 kcal · mol^{-1}.

On this basis we would expect 1-indenyl complexes having a facile decomposition path whose activation energy is significantly less than 13 kcal · mol^{-1} to decompose before the onset of measurable fluxional behaviour** [although such behaviour might be demonstrable in such systems by experiments designed to trap the intermediate (II)]. Those lacking such a decomposition path should exhibit [1, 3] averaging, *via* (II), with an activation energy of at least 13 kcal · mol^{-1}. This prediction may be compared with the available experimental activation energies for [1, 3] averaging; 12.9 ± 0.6 (bisindenylmercury)[14], 14.1 ± 0.4 [1-(dimethylphenylstannyl)inde-

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* A similar treatment of the resonance energy of benzene by union of methylene with pentadienyl yields a value of $2\beta/\sqrt{3}$. Accepting Dewar's critique of resonance energies, and his value of 20 kcal · mol^{-1} for that of benzene[12] $\beta \sim 17.3$ kcal · mol^{-1}.

** A possible example is $(h^5\text{-}C_5H_5)(h^1\text{-}C_9H_7)(CO)_2Fe$[13].

ne][15], 14.2±0.7 [1,3-dimethyl-1-(trimethylstannyl)indene][15], 22 [1-(trimethylgermyl)indene][6], < 29 [1-(trimethylsilyl)indene][6], 23.0±1.6 [1-(dimethylphenylsilyl)-indene][15] and 26.1±1.4 kcal·mol^{-1} [1,2-bis(trimethylsilyl)indene][15] (III). As expected for the intermediacy of (II), none is significantly less than 13 kcal·mol^{-1}. Persuasive evidence for the involvement of intermediates resembling (II) has also been provided by qualitative[6] and quantitative[7] trapping experiments.

Finally we extend the ideas developed above to consider the possibiliby of *simultaneous* [1, 2] shifts in alternant hydrocarbon complexes containing more than one sigmatrope. Such a process has been suggested[15] as an alternative to sequential [1, 2] shifts in compound (III). In the transition state for a single shift one carbon p orbital is removed from the delocalized system leaving an odd alternant p_π network. Such a network is required by the pairing theorem[10] to have an NBMO and is thus energetically suitable for strong first order interaction with the critical orbital of the migrating system (*vide supra*). In the transition state for a double shift, two p orbitals would be removed from the delocalized system leaving an even alternant p_π network. Such a network will not, in general, have an NBMO*, and a transition state of this type will lack strong first order stabilization. It should, for this reason, lie at higher energies than the transition state for a single shift.

In the case of (III), for example, the transition state for simultaneous [1, 2] shifts would have an adjacent p_π system resembling benzene, which clearly would lack an NBMO. Therefore, of the two averaging processes proposed for (III), that involving sequential [1, 2] shifts is preferred by the present approach.

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* The pairing theorem requires an NBMO in a neutral even alternant hydrocarbon to be doubly degenerate and half occupied. It should thus be subject to strong first order Jahn–Teller distortion.