common acceptor are predicted to become shorter as they get stronger, in agreement with available data. C–H donors show some attraction for most neutral acceptors, but it is not clear whether these interactions should be classified as H bonds. (iv) H bonds to a common donor are predicted to become stronger in the acceptor order $\mathrm{Ne} < \mathrm{FH} < \mathrm{OH_2} \lesssim \mathrm{N\,(HCN)} < \mathrm{N}$ $(\mathrm{NH_3}) < \mathrm{F^-}$. They are also predicted to become shorter in the same order, which (except for F^-) is not observed in recent SCF calculations. In addition to the electronegativity of the acceptor atoms, the size of the acceptor atom and the local asymmetry of its lone-pair electron distribution are found to be of importance in determining the acceptor strength. (v) "H bonds" to Ne are little affected by varying the donor, and in all cases the potential curve is repulsive. (vi) H bonds to an atom B are predicted to become weaker and longer as the lone-pair s character of B increases. Thus amines are better acceptors than nitriles, and ethers should be better acceptors than ketones. (vii) Steric requirements for H bonding to N, O, and F are found to differ considerably, N in amines giving good H bonds only for an approach along the N lone-pair axis. For O and F acceptors, the optimum direction of approach depends sensitively on the lone-pair s character. (viii) Many of the trends in stability discussed above can be rationalized by considering changes in the electrostatic energy alone. This is also true for the optimum orientations adopted by the acceptor in linear $\mathrm{A{-}H\cdots B}$ bonds, providing that one goes beyond the usual dipole–dipole approximation.

Acknowledgment. We thank Professor D. H. W. den Boer for his interest in this work and for critically reading the manuscript. We thank Dr. P. J. A. Ruttink for running the computer program while we were on leave.

Extended Woodward–Hoffmann Rules for Sigmatropic Rearrangement of Stereochemically Nonrigid Organometallic Compounds with Carbon–Metal σ Bonds

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Abstract: A combination of energy level correlation diagrams and a simple perturbation method indicates that the rearrangement pathways (under thermal conditions) of fluxional organometallics with carbon–metal σ bonds are governed by the highest occupied molecular orbital of the organic portion of the transition state. This conclusion is in accord with the Woodward–Hoffmann rules for sigmatropic rearrangements. With additional consideration of the metal moieties, guidelines are established which correlate specific pathways involved in fluxional behavior.

Cotton and coworkers[1,2] have examined the dynamic processes of some fluxional organometallic compounds. Fluxional behavior is a set of concerted displacements of the metal from one carbon to another. This paper attempts to relate the fluxional behavior of some organometallics, which contain one metal group σ bonded to a π-conjugated organic portion, to the Woodward–Hoffmann rules[3,4] for sigmatropic rearrangements of organic compounds.[5]

Two steps are necessary. First, energy correlation diagrams[6a] are constructed. Then the detailed rearrangement pathway is treated by a simple perturbation method.[6b]

Correlation Diagrams

Consider, for example, $(h^1\text{-}\mathrm{C_5H_5})\mathrm{M}$, in which M is the migrating moiety. The symmetry planes of the molecule and the transition state are shown in Figure 1.

In the rearrangement, six orbitals of $(h^1\text{-}\mathrm{C_5H_5})\mathrm{M}$ change, namely, σ, σ^*, ψ_1', ψ_2', ψ_3', and ψ_4'. Here σ and σ^* are the bonding and antibonding orbitals of the carbon–metal σ bond and the latter four orbitals are the conjugated diene molecular orbitals. The corresponding six orbitals in the transition state are $\mathrm{M_s}$, ψ_1, ψ_2, ψ_3, ψ_4, and ψ_5. Here $\mathrm{M_s}$ is the orbital of the migrating metal and the latter five orbitals are those of the cyclopentadienyl group. Table I gives the symmetries of the orbitals. Charts I–VI give the correlation diagrams of the orbitals as the $\mathrm{M_s}$ energy level varies.

In these diagrams, the $\mathrm{M_s}$ orbital is an A′ orbital (*i.e.*, it is symmetric with respect to the symmetry plane); examples are s, p_x, p_y, and certain hybrid orbitals of the M atom, depending upon its valence shell.

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[1] F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968), and references therein.

[2] M. T. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, 88, 4371 (1966).

[3] R. B. Woodward and R. Hoffmann, *ibid.*, 87, 2511 (1965).

[4] R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

[5] For additional applications of the Woodward–Hoffmann rules to the reactions of transition metal complexes, see, for example, (a) D. R. Eaton, *J. Amer. Chem. Soc.*, 90, 4272 (1968); (b) T. H. Whitesides, *ibid.*, 91, 2395 (1969); (c) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, 92, 3515 (1970). None of these treatments applies to reversible sigmatropic arrangements.

[6] (a) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2045 (1965); (b) H. E. Zimmerman, D. S. Crumrine, D. Dopp, and P. S. Huyffer, *ibid.*, 91, 434 (1969).

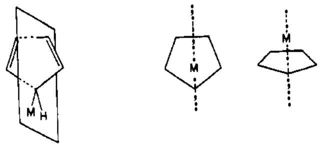


Figure 1. The symmetry planes of (h^1-C_5H_5)M and the transition state.

The correlation diagrams tell us that the thermal process is accessible only if the M_s energy level is higher than the HOMO of the conjugated organic moiety in the transition state and that the thermal process is governed by the HOMO of the organic part in the transition state (in accordance with the Woodward–Hoffmann rules of sigmatropic rearrangement).

For other C_s symmetrical molecules, previous procedures are feasible. However, it is impossible to construct correlation diagrams for molecules which have no symmetry plane, or for the case when M_s is an antisymmetrical orbital in the transition state. The diagrams also cannot distinguish between a 1,2 shift and a 1,3 shift[7] because both are symmetry allowed. To determine the specific pathway, a simple perturbation method is employed.

Perturbation Method

Zimmerman[6b] derived an equation for the splitting of the energy levels of two interacting molecular orbitals.

$$E_{\pm} = (^1/_2)(E_u + E_l) \pm (^1/_2)\sqrt{(E_u - E_l)^2 + B} \quad (1)$$

$$B = 4(\sum_i \sum_j C_{iu}C_{jl}h_{ij})^2$$

E_+ and E_- are the split energy levels resulting from the interaction of the two MO's, ψ_u and ψ_l, the h_{ij}'s are the matrix interaction elements

$$h_{ij} = \int \phi_i H' \phi_j d\tau$$

and B is a measure of the extent of the interaction. To apply eq 1 to the rearrangements, take ψ_u and ψ_l as, respectively, the lowest unoccupied orbital and the highest occupied orbital of the transition state. Hence, the larger the value of B, the larger the splitting of the two energy levels and the more the transition state will be stabilized.

When the lobe(s) of the atomic orbital of the M_s and the lobes of the interacting carbon atoms of the HOMO in the transition state have the same sign, B will be large. Figure 2 shows schematically the stabilized transition states. If there are more than two shifts accessible by symmetry arguments, the magnitude of B can be used to determine the favorable process. To illustrate this method, consider (h^5-C_5H_5)(CO)$_2$Fe(h^1-C_5H_5). The HOMO of the cyclopentadienyl group is

$$\psi_3 = 0.599\phi_1 + 0.370\phi_2 - 0.370\phi_3 - 0.599\phi_4$$

Since this is a concerted process, the interactions of the metal orbital and the two carbon orbitals of the exchanging sites are large. Other interactions are negligible. Assuming the rearrangement is from C_1 to C_2 for a 1,2 shift, then

$$B = 4(C_mC_1h_{mc} + C_mC_2h_{mc})^2$$

If the rearrangement is from C_1 to C_3 for a 1,3 shift, then

$$B = 4(C_mC_1h_{mc} + C_mC_3h_{mc})^2$$

Table I. Symmetries of the Orbitals

Symmetry	(h^1-C_5H_5)M	Transition state
A′	σ, σ^*, ψ_1', ψ_3'	M_s, ψ_1, ψ_2, ψ_4
A″	ψ_2', ψ_4'	ψ_3, ψ_5

Chart I

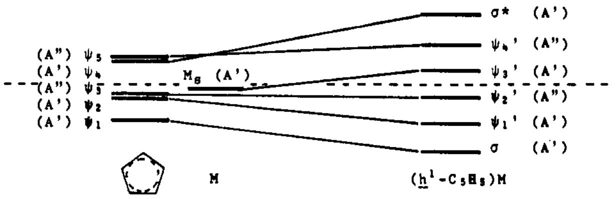


Chart II. Correlation Diagram for the M_s Energy Level Higher than the ψ_3 Energy Level

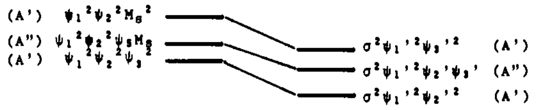


Chart III

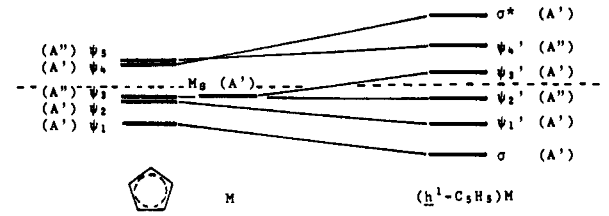


Chart IV. Correlation Diagram for the M_s Energy Level Equal to the ψ_3 Energy Level

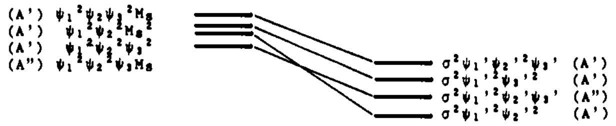


Chart V

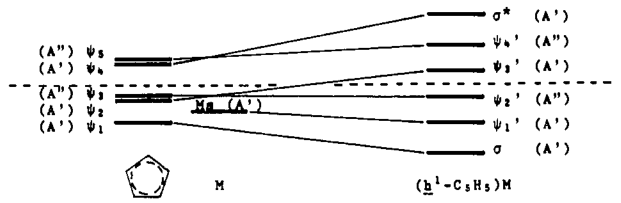
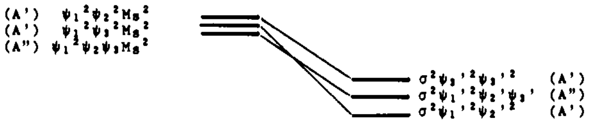


Chart VI. Correlation Diagram for the M_s Energy Level Lower than the ψ_3 Energy level



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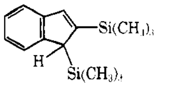
[7] For example, see (a) ref 2; (b) F. A. Cotton, A. Musco, and G. Yagupsky, *J. Amer. Chem. Soc.*, **89**, 6136 (1967); (c) F. A. Cotton and T. J. Marks, *ibid.*, **91**, 7523 (1969); (d) J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *ibid.*, **92**, 3801 (1970).

Table II. Comparisons between Predicted and Observed Fluxional Character of Organometallic Derivatives

Compound	Class	Predicted shift	Observed shift	Ref
$(h^5\text{-}C_5H_5)(CO)_2Fe(h^1\text{-}C_5H_5)$	I	1,2 (rule 1)	1,2	2
$(h^5\text{-}C_5H_5)(NO)_2Cr(h^1\text{-}C_5H_5)$	I	1,2 (rule 1)	1,2	7b
$(h^5\text{-}C_5H_5)(CO)_2Ru(h^1\text{-}C_5H_5)$	I	1,2 (rule 1)	1,2	7c
$(h^5\text{-}C_5H_5)((NO)Mo(h^1\text{-}C_5H_5)$	I	1,2 (rule 1)	1,2	7b, 7c
$(h^5\text{-}C_5H_5)_2Ti(h^1\text{-}C_5H_5)_2$	I	1,2 (rule 1)	1,2	7b, *a*
$(h^5\text{-}C_5H_5)(CO)_2Fe(h^1\text{-}C_9H_7)$	I	nf (rule 2b)	nf[b]	7b
$(h^1\text{-}C_9H_7)_2Hg$	II	1,3 (rule 2b)	1,3	*c*
$(h^1\text{-}C_5H_5)_2Hg$	II	1,2 (rule 1)	fl[d]	*e*
$(h^1\text{-}C_9H_7)HgCl$	II	1,3 (rule 2b)	nf	*f*
$(h^1\text{-}C_5H_5)HgCl$	II	1,2 (rule 1)	fl	*f*
$(h^1\text{-}C_9H_7)Li$	II	1,3 (rule 2b)	fl	*f*
$(h^1\text{-}C_5H_5)AuP(C_6H_5)_3$	II	1,2 (rule 1)	fl	*g*
$(h^1\text{-}C_5H_5)Si(CH_3)_3$	III	1,2 (rule 1)	1,2	*h*
$(h^1\text{-}C_5H_5)Ge(CH_3)_3$	III	1,2 (rule 1)	1,2	*h*
$(h^1\text{-}C_5H_5)_4Sn$	III	1,2 (rule 1)		*h*
$(h^1\text{-}C_9H_7)Si(CH_3)_3$	III	1,2 (rule 3)	1,2	*h, i*
	III	1,2 (rule 3)	1,2	*i*
$(h^1\text{-}C_9H_7)Ge(CH_3)_3$	III	1,3 (rule 2b)	1,3	*i, j*
$(h^1\text{-}C_9H_7)Sn(CH_3)_3$	III	1,3 (rule 2b)	1,3	*j*

[a] F. W. Siegert and H. J. de Liefde Meijer, *J. Organometal. Chem.*, **20**, 141 (1969). [b] nf represents nonfluxional. [c] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 3178 (1969). [d] fl represents fluxional. [e] E. Maslowsky and K. Nakamoto, *Chem. Commun.*, 257 (1968). [f] W. Kitching, B. F. Hegarty, and D. Doddrell, *J. Organometal. Chem.*, **16**, P39 (1969). [g] W. Kitching, B. F. Hegarty, and D. Doddrell, *ibid.*, **21**, 29 (1970). [h] H. P. Fritz and C. G. Kreiter, *ibid.*, **4**, 313 (1965). [i] A. Davison and P. E. Rakita, *ibid.*, **21**, P55 (1969). [j] P. E. Rakita and A. Davison, *Inorg. Chem.*, **8**, 1164 (1969).

where C_m is the coefficient for the metal orbital and h_{mc} is positive. The largest B value will be obtained when C_1 is 0.370 and C_2 is 0.599. Therefore, a 1,2 shift is favored.

Although the correlation diagram is restricted to C_s symmetrical molecules, the second method is applicable to both symmetrical and unsymmetrical molecules. The generalizations deduced from the symmetry consideration are assumed to be applicable to unsymmetric molecules.[8]

Conclusions

Since the energy level of the migrating system should be higher than the HOMO, the metals considered[10] will be the Li, Be, some transition metals, group IVa and members of group Va (As, Sb, and Bi), and group VIa (Te and Po), which are divided into three classes according to the possible structures of the compounds.

Class I, including groups IIIb, IVb, Vb, VIb, VIIb, and VIII, can migrate only from a positive to a positive lobe (as in Figure 2, **1**). Because of steric hindrance, there will be little or no inversion during the rearrangement.

Class II, including groups Ib, IIb, and IIIa and Li and Be, can migrate from a positive to a positive or a positive to a negative lobe. Because there are low-lying empty orbitals, the transition state can use either the originally bonded orbital (as in Figure 2, **1**) or the empty orbitals by expanding the valence shell (as in Figure 2, **2**).

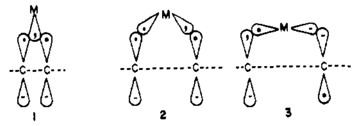


Figure 2. The stabilized transition states (schematic). In **1**, the metal lobe is a hybrid orbital developed from the originally bonded lobe. In **2**, one metal lobe represents that developed from the originally bonded lobe and another is one of the low-lying p orbital lobes. In **3**, the metal orbital is a p orbital.

Class III, including group IVa and part of groups Va and VIa, can migrate from a positive to a positive or a positive to a negative lobe, because the originally bonded lobe (as in Figure 2, **1**) or the inversion of the originally bonded lobe (as in Figure 2, **3**) can be used in the transition state.

The general rules for thermal rearrangements are as follows. (1) If there are adjacent positive centers (or lobes),[11] members of classes I, II, and III undergo adjacent shifts (fluxional). (2) If there are no adjacent positive centers, but (a) there are nonadjacent positive centers,[11] then members of classes I, II, and III undergo nonadjacent shifts (fluxional). If (b) there are adjacent positive–negative centers,[11] then members of class I are nonfluxional, but classes II and III are fluxional. (3) If there are nodes adjacent to positive centers,[11] only the compounds which are stable with the migration moiety on these nodes are expected to be fluxional.

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(8) Although this assumption is not proved here, the present treatment may be extended in a manner closely analogous to that used by Woodward and Hoffmann[4] as applied to sigmatropic rearrangements. The three qualitative methods suggested by Woodward and Hoffmann[9] are just as useful to prove the fluxional behavior of organometallic compounds as to prove the sigmatropic rearrangement of organic compounds.

(9) R. B. Woodward and R. Hoffmann "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 114–118.

(10) The organometallic compounds of groups Ia and IIa, except Li and Be, are essentially ionic and are not considered here. Because the ionization potentials of the compounds of Sc, Y, As, and Te have not been reported, decisions were made for these cases on the basis of metal electronegativities. This treatment is not extended to compounds of the inner transition metals.

(11) Here, regard the coefficients of the HOMO of the organic portion in the transition state. One of the positive lobes is that of carbon originally bonded to the metal group.

Discussion

Interest in the structural behavior of organometallics has persisted for several years. A number of fluxional compounds have been examined in order to probe the structural basis for fluxional behavior. This paper presents elements leading toward a rationale for such behavior. In addition to defining the scope of the migrating group, it summarizes the argument that the rearrangement pathway is governed by the HOMO of the organic group in the activated complex.

Table II shows the agreement between the predicted and observed fluxional shifts associated with compounds described in recent years. The chloromercurial derivative (h^1-C_9H_7)HgCl has been reported to be nonfluxional at 33°, in conflict with the present predictions. Note, however, that the temperature of nmr line broadening for (h^1-C_5H_5)$_2$Hg (−70°) is over 100° below that for its chloromercury analog, (h^1-C_5H_5)HgCl (+33°). Since the broadening temperature for the bisindenyl derivative, (h^1-C_9H_7)$_2$Hg, is reported as −3°, it is not unreasonable to suppose that temperatures well above 33° are necessary for fluxional behavior in its chloromercury counterpart. Further work, at higher temperatures, would be of interest here.

The rearrangement of some compounds reported by Fritz and Kreiter[12] is consistent with the present treatment. However, more certain identification of the rearrangement pathway appears to be desirable.

Note that all compounds in Table II feature indenyl and cyclopentadienyl groups. Further study of fluxional compounds derived from additional organic systems, to corroborate the present treatment, is obviously desirable.

Acknowledgements. The author wishes to thank Professors E. S. Gould and D. F. T. Tuan for their encouragement and valuable discussion.

(12) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **4**, (313) (1965).

Cyclopentadienylcopper(I)–Isocyanide Complex. A New Preparative Method and Catalyst Activity

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Abstract: (*pentahapto*-Cyclopentadienyl)(*tert*-butyl isocyanide)copper(I) (**1**) and (indenyl)tris(*tert*-butyl isocyanide)copper(I) (**2**) were readily prepared by the reactions of cyclopentadiene and indene, respectively, with the Cu_2O–*tert*-BuNC system. These organocopper(I) complexes catalyzed the reactions of cyclopentadiene homologs with carbonyl compounds, producing the corresponding fulvene derivatives **3**. The catalytic activity of **1** was much increased by the addition of an equimolar amount of *tert*-BuNC. For catalysis of these reactions, it was not necessary to isolate an organocopper complex; *i.e.*, these reactions were effectively catalyzed by the Cu_2O–*tert*-BuNC system. In addition, the Cu_2O–*tert*-BuNC system catalyzed the reactions of active hydrogen compounds such as malonate with aldehyde affording the corresponding alkylidene malonate derivatives.

The present paper is concerned with organocopper(I)–isocyanide complexes derived from cyclopentadiene homologs, Cu_2O, and isocyanide. In recent years, much attention has been paid to the usefulness of organocopper reagents in organic syntheses[1] as well as the characterization of organocopper compounds.[2] For several years, we have devoted ourselves to studies of catalytic activity of Cu(I)–alkyl isocyanide complexes.[3] Characteristic catalytic activity of the Cu(I)–isocyanide system has been demonstrated in reactions involving so-called active hydrogen compounds, such as the dimerization of α,β-unsaturated carbonyl and nitrile compounds[4a,b] (eq 1), Michael-type addition reactions,[4c] and cycloaddition of benzyl and carboalkoxymethyl isocyanides[4d] (eq 3 and 4). In these reactions, we assumed a reaction scheme with an organocopper (I)–isocyanide complex as active intermediate.

The present paper reports the preparation of (*pentahapto*-cyclopentadienyl)(*tert*-butyl isocyanide)copper(I) (**1**) and (indenyl)tris(*tert*-butyl isocyanide)copper(I) (**2**) by the reactions of cyclopentadiene and indene, respectively, with the Cu_2O–*tert*-BuNC system. These organocopper complexes were found to be key intermediates in reactions of cyclopentadiene homologs with carbonyl compounds, catalyzed by the Cu_2O–isocyanide system. In addition, complex **1** was found to catalyze reactions 1 and 2.

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(1) (a) E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967); (b) E. J. Corey and G. H. Posner, *ibid.*, **90**, 5615 (1968); (c) E. J. Corey and J. A. Katzenellenbogen, *ibid.*, **91**, 1851 (1969); (d) J. B. Siddal, M. Biskup, and J. H. Fried, *ibid.*, **91**, 1853 (1969); (e) E. J. Corey and I. Kuwagima, *ibid.*, **92**, 395 (1970); (f) R. J. Anderson, C. A. Henrick, and J. B. Siddall, *ibid.*, **92**, 735 (1970).

(2) (a) F. A. Cotton and T. J. Marks, *ibid.*, **91**, 7281 (1969); (b) F. A. Cotton and J. Takats, *ibid.*, **92**, 2353 (1970); (c) G. M. Whitesides and J. S. Fleming, *ibid.*, **89**, 2855 (1967); (d) F. A. Cotton and T. J. Marks, *ibid.*, **92**, 5114 (1970).

(3) (a) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota and H. Yoshioka, *Bull. Chem. Soc. Jap.*, **42**, 3310 (1969); (b) T. Saegusa, Y. Ito, S. Kobayashi, J. Hirota, and N. Takeda, *Can. J. Chem.*, **47**, 1217 (1969); (c) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *J. Amer. Chem. Soc.*, **89**, 2240 (1967).

(4) (a) T. Saegusa, Y. Ito, S. Tomita, and H. Kinoshita, *J. Org. Chem.*, **35**, 670 (1970); (b) T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, *Bull. Chem. Soc. Jap.*, **43**, 877 (1970); (c) T. Saegusa, Y. Ito, S. Tomita, and H. Kinoshita, *ibid.*, in press; (d) T. Saegusa, Y. Ito, S. Tomita, and H. Kinoshita, *J. Org. Chem.*, in press.